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and the

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TECHNIQUE FOR THE EXTRACTION AND PARTIAL CHEMICAL ANALYSIS OF FLUID-FILLED INCLUSIONS FROM MINERALS [1]

EDWIN ROEDDER

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ABSTRACT

A method has been developed for the extraction and limited chemical analysis of the materials in solution in the fluid from the very minute

[1] Publication authorized by the Director, U. S. Geological Survey.

fluid-filled inclusions such as commonly occur in whitish or milky quartz. The method may also be applied, with some reservations, to a variety of other minerals. As the amounts of substances in the fluid are small compared with possible contaminants, great care is needed in sample purification and cleaning; an electrolytic method has been found to be the only satisfactory final cleaning step. Following this, the inclusions are opened by ball milling of the cleaned sample, with deionized water, in an alumina ball mill using alumina grinding media. The ions present in the resultant slurry are separated from the ground quartz by electrodialysis and analyzed. Other methods, such as the decrepitation of a sample in an absorption train, are used to estimate the amount of H_2O and CO_2 in the inclusions. The most significant part of the analytical work has been to determine the ratios between the alkali metals.

The materials in solution in the fluid-filled inclusions from 11 samples of quartz have been analyzed by the ball milling-electrodialysis method. Although there are large differences between samples, the *average* weights of the alkali metal ions found, for all samples, in milligrams per kilogram of quartz, are: Li^+—0.92, Na^+—99, K^+—133, Rb^+—0.45, Cs^+—0.38 (atomic ratios, in the same sequence: 0.03/1.00/0.79/0.001/0.0007). In addition, 27 to 193 milligrams of Cl^-, and 5 to 140 milligrams of $SO_4^=$ were found, per kilogram of quartz. H_2O and CO_2 were determined on only one sample. Six of the samples were from gold-quartz veins in the Grass Valley district, California. In these six the Na^+/K^+ ratios were all very similar, but the amounts of Li^+, Rb^+ and Cs^+ found varied greatly.

Although there are serious limitations to this and to all other techniques developed, it is felt that the results presented are sufficiently encouraging to warrant further study and possible application to specific geologic problems, such as the identification of epochs of quartz deposition.

INTRODUCTION

PRACTICALLY all minerals from rocks other than unaltered lavas contain some fluid-filled inclusions, but as most inclusions are less than 2 microns in size, they have been ignored in most routine mineralogical studies. Much work has been done in the past on the composition of the fluid in large inclusions, where the contents of a single inclusion or "vacuole" were easily removed and adequate for analysis. Inclusions of this type are mineralogical rarities (31); if much is to be learned about the composition of the fluids from which minerals have been deposited or recrystallized, it is necessary to study a type of inclusion that is much more abundant. This paper describes a method that has been developed for the extraction and partial chemical analysis of the fluid from the ordinary, minute inclusions in kilogram samples of minerals. For reasons discussed beyond, most of this work has been performed on quartz, although similar procedures might be used on beryl, topaz, fluorite, etc.

The present method of extraction leaves much to be desired, and even if a perfect method were developed, the interpretation of the results would be subject to serious limitations, in particular the possibility of multiple generations of inclusions in a sample, and the possibility of loss or gain of materials by leakage or diffusion. There has been considerable discussion in the literature on the origin and significance of these inclusions, which will be considered in this paper only insofar as they influence the technique used. Regardless of how and when they were formed, and how they might have changed since

that time, inclusions do represent samples of fluids existing in nature at some time in the past, and as such they merit study to determine what they might reveal about long-past geologic processes and conditions. It seems logical that with the development of an adequate extraction technique, this very ambiguity of origin may be investigated and become helpful in delineating the history of a sample or region. In any case, even though the method remains capable of yielding only meager data, such data on the composition of the fluids from which minerals have grown or recrystallized in nature are otherwise unobtainable and may possibly prove of value in several ways. One example is in the field of geologic thermometry, where the differences between KCl and NaCl solutions, as well as the concentrations, are very important; see Bowen (3, p. 195), and Ingerson (34, p. 378). The study of the significance of the composition of the fluid in these fluid-filled inclusions in minerals, and of the possible application of the analytical results to the solution of geologic problems, is continuing.

This work, supported in part by a contract with the Office of Naval Research, was started in 1948 while the author was at Columbia University; later, at the University of Utah, it was supported in part by contracts with the Office of Naval Research and with the United States Army Signal Corps Engineering Laboratories,[2] and a grant from the National Science Foundation. I also wish to acknowledge a grant in 1954 from the University of Utah Research Committee.

I am indebted to a number of undergraduate and graduate students at the University of Utah, in particular Kenneth Larsen, William B. Phillips, and Lloyd L. Ames, Jr., who were employed part-time to perform much of the tedious work of sample preparation and ball milling, under the several contracts. Most of the actual runs and analytical determinations reported here were made by Dr. Ames, under the Signal Corps contract, and I particularly wish to express my gratitude to him for this work.[3]

NATURE OF THE PROBLEM

Most natural quartz samples are translucent, rather than transparent because they contain large numbers of minute liquid-filled inclusions that scatter light. In a very few samples this milkiness may be due to exsolution of impurities on cooling (A. J. Cohen, Mellon Institute, oral communication, May, 1957), or to minute solid inclusions trapped during the growth of the crystal. Although quartz itself is perfectly transparent, and the fluid-filled inclusions generally contain only transparent liquid and vapor phases, there are sizable differences in the index of refraction of these three phases that result in light scattering. Where inclusions are particularly abundant, the quartz is milky. The whiteness of a sample is only a very crude measure of

[2] A considerable part of this work was originally given by the author in the final report to the Signal Corps, dated Feb. 15, 1954, on contract DA 36–039, SC–42635, entitled "Composition and Significance of Fluid Filled Inclusions in Quartz and Other Minerals," University of Utah, 1954.

[3] Since the author left Utah, Mr. Ames continued independent work with the technique for his doctoral research, the results of which will be published in this Journal.

the amount of liquid. The volume of spherical inclusions varies as the cube of the radius, so the total volume of liquid present in a given sample will be increased drastically by the presence of a very few large inclusions, as shown in Figure 1; these would have very little effect on the whiteness.

These inclusions are, for the most part, very minute. Although most quartz crystals contain fluid inclusions, with vapor bubbles, that can be seen with the aid of a good hand lens (i.e., larger than 40μ), most of the inclusions

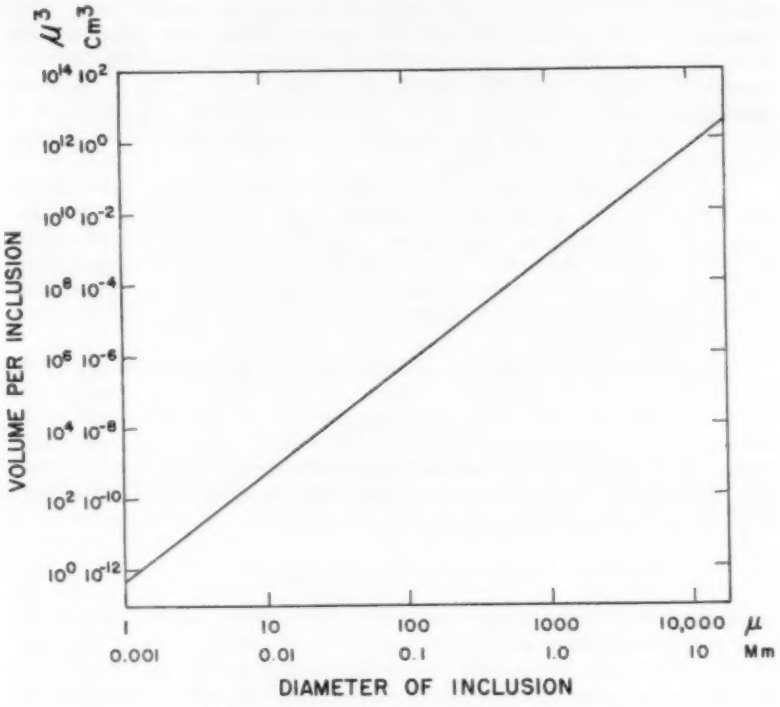

FIG. 1. Volume of spherical inclusions.

are 2μ or less in diameter, and hence cannot be seen without the use of high magnifications. The number of such inclusions is surprisingly large; a crude count of representative volumes of several vein quartz samples, made by using a grid ocular and the fine adjustment screw on the microscope, showed of the order of 10^9 such inclusions per cm^3,[4] yet these samples would be classed as translucent rather than milky. Since the inclusions average a little more than 1μ in size, there would be approximately 0.1 percent fluid, by volume, in these

[4] Vogelsang (63) found more than 10^{11} liquid inclusions per cm^3 in the quartz of a granite, and Zirkel (69) reports an estimate of 3.6×10^{11} gas-filled inclusions per cm^3 in hauynite.

samples.[5] A one-kilogram sample would thus contain approximately 1 cm^3 of solution, and as shown beyond, this solution would contain tens or hundreds of milligrams of salts.

The problem, then, is simply to open these tiny "quartz bottles," extract the fluid, and analyze it. The main difficulty lies in avoiding contamination from a variety of sources, and, to a lesser extent, in reducing losses. In order to overcome difficulties introduced by variation in the amount of inclusions in the samples and by variable efficiency of extraction, most of the work has been aimed at determination of the *ratios* between specific ions rather than at determination of absolute amounts. A tentative goal was the development of a process that would open more than 90 percent of the inclusions in the sample, and would recover more than 90 percent of the ionizable salts from the opened inclusions.

PREVIOUS WORK

Much work has been done in the last hundred years on fluid inclusions in minerals, for a variety of reasons, and the rather voluminous literature on the subject has been gathered together in an annotated bibliography by Smith (55). It is interesting to note that intensive studies of fluid inclusions were first undertaken in order to provide evidence for the Neptunist or Plutonist theories of the origin of crystals in rocks (for example, Brewster, 6).

Many of these studies have involved attempts to determine the composition of the fluid in the inclusions, but most of the work has been on single, large inclusions. The most direct method, that of drilling into a large inclusion, or "vacuole," was used in work reported by Breislak in 1818 (5), and Davy (17), and similar studies, including even pH determinations, have been made by many others (36). Additional studies of the composition of the fluids in unopened inclusions have been made by a variety of ingenious methods, including the determination of total reflection angles, of thermal expansion coefficients, and of phase relationships on freezing and heating (including critical phenomena). Decrepitation in a spectroscope, and, of course, simple crushing and leaching have also been used. Many of these techniques were first described, and the validity of their results carefully interpreted, in the classic study of fluid inclusions by H. C. Sorby just 100 years ago (56). He designed many significant experiments, and in fact, a number of later discoveries concerning the geological significance of fluid inclusions and the phase relationships of the materials in them were anticipated by Sorby in his 1858 paper and in some of his later publications. The meticulous observations of Sorby, and later of Zirkel (69) in his careful studies of practically all observable microscopic features of rocks collected during the geological investigation of the 40th parallel of the United States, have shown that the dominant material in fluid inclusions is a rather concentrated and at times saturated water solution of various salts, in particular sodium and potassium chloride, and, in some, free CO_2.

Recent studies by Weis (66), and Cameron, Rowe, and Weis (12), using

[5] Sorby (56) reports that he found 1 percent, by volume, of fluid inclusions in the quartz of the Cornwall granite, and a few samples with as much as 2 percent, by weight, have been reported (55, p. 89).

freezing point depression measurements, and by Wahler (64), using index of refraction measurements and leaching of decrepitated inclusion samples, indicate the solutions in the fluid inclusions in pegmatite minerals to be up to 5 molar (as NaCl). Many localities yield inclusions showing solid cubic crystals of an isotropic material, presumably KCl or NaCl (55), and such crystals are particularly common in the fluid inclusions from late differentiates of granitic rocks, such as porphyries (46, p. 425).

In some of the studies, crushing, followed by leaching, was used to obtain the composition of the salts in comparatively small samples of minerals containing rather large inclusions (for example, Salm-Horstmar, 52; Konigsberger and Muller, 39, 40; Newhouse, 46). Lamar and Shrode (42) obtained the fluid inclusions in large samples of limestone and dolomite by grinding and leaching. Large samples of igneous and metamorphic rocks were ground and leached by Faber (22). As Faber points out, however, it is impossible with this method to differentiate alkalies dissolved from the minerals of the rock itself and those from inclusions, if alkali-bearing minerals such as feldspar are present. If sulfides were present in these rocks, it would be difficult to avoid oxidation by atmospheric oxygen during the four- to six-week leaching used by Faber. Faber felt that the chloride obtained (several hundred milligrams from two kilograms of rock) came from the inclusion liquid. Little is known concerning the mineralogy of chlorine in granites, except that at least some of it occurs in fluid inclusions. Although there are some chlorine-bearing rock minerals, it would be possible to have the entire amount of chlorine in rocks (averaging 300 ppm) occur in fluid inclusions, as 0.2 percent of liquid containing 15 percent Cl^- would account for it. Pure quartz was used in the present study to avoid these possibilities of ambiguity.

Recently, Umova, Glebov, and Shibanov (61), ground quartz crystals in a ball mill connected with a high-vacuum apparatus to collect the evolved gases for analysis. They found up to nearly 0.5 percent by weight of $H_2O + CO_2$, but apparently they did not analyze for nonvolatile soluble salts.

DESCRIPTION OF THE BALL MILLING-ELECTRODIALYSIS TECHNIQUE

Sample Purification and Cleaning.—The importance of this cleaning step cannot be overestimated, because the amount of salts in solution in the liquid inclusions is only of the order of tens or hundreds of milligrams per kilogram of quartz. As a result great care must be taken, prior to the ball milling, to free the quartz completely from adsorbed ions on the surface, soluble salts in cracks, and any other minerals such as feldspar that might release ions into the solution.

The process used is varied with the nature of the sample, but usually starts with careful hand sorting in the field, acid washing to remove limonite stains that might conceal other minerals, crushing to minus ½ inch, and additional hand sorting to remove minerals other than quartz, followed by several passes through rolls to reduce the sample to $-10+48$ mesh. Adhering fines are washed out and two bulk separations with heavy media (Thoulet's solution) are performed to obtain the fraction having grain densi-

ties between 2.575 and 2.645 g/cm³. This procedure eliminates most other minerals and also most of the clear quartz grains, of slightly higher density, containing relatively few inclusions (Fig. 2). Samples containing albite-rich plagioclase could not be purified by this procedure and were not run. Small amounts of other minerals, such as stains of limonite and attached grains of carbonate, are then removed with boiling HCl. (If sulfides are still present, the sample is boiled with HNO_3 or aqua regia, washed, and baked overnight at ∽100° C to vaporize the precipitated sulfur.) After washing to remove most of the acid, the quartz is put into large glass leaching jars and leached continuously for several days with a flow, first of tap water, then distilled water, and finally deionized water, to remove most of the salts from ground

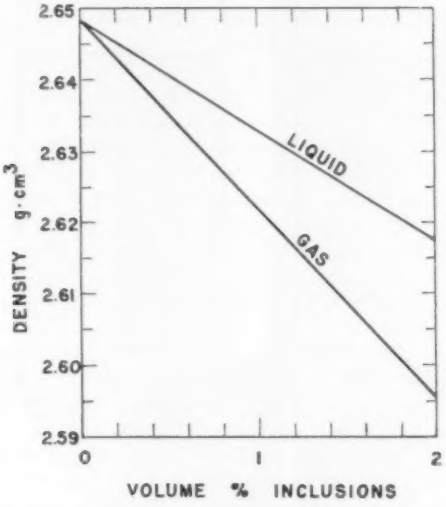

FIG. 2. Variation in density of quartz (calculated) from presence of fluid-filled inclusions containing liquid (density—1.1) and gas (density—0.0). Density of pure quartz taken as 2.6484 (Frondel and Hurlbut, 24).

water and leaching acids from the cracks in the individual grains. Then, to remove the last traces of ionizable materials, including those adsorbed on surfaces, the quartz is washed into an electrolytic cleaning cell[6] (Fig. 3), where it is covered with deionized water, and 90 volts direct current is applied to the platinum electrodes. In general the initial current flow will be about 0.1 milliampere and will rise to about 0.2 ma as additional ions diffuse off surfaces and out of cracks, and increase the conductivity of the deionized water.[7]

[6] This exceedingly useful technique was suggested to the author by Prof. C. E. Marshall of the University of Missouri, to whom I wish to express my appreciation.

[7] By using distilled water and a mixed-bed resin deionizer the exit water from the deionizer is freed of ions sufficiently to have a resistance of greater than 250,000 ohms/cm³.

The applied potential drives ionizable substances to the vicinity of the electrodes. As soon as an approximation to equilibrium obtains between the concentration of ions in the water surrounding the electrodes and the diffusion of these ions away from the electrodes, as shown by constant current flow, the water around the electrodes is poured off quickly and that between the

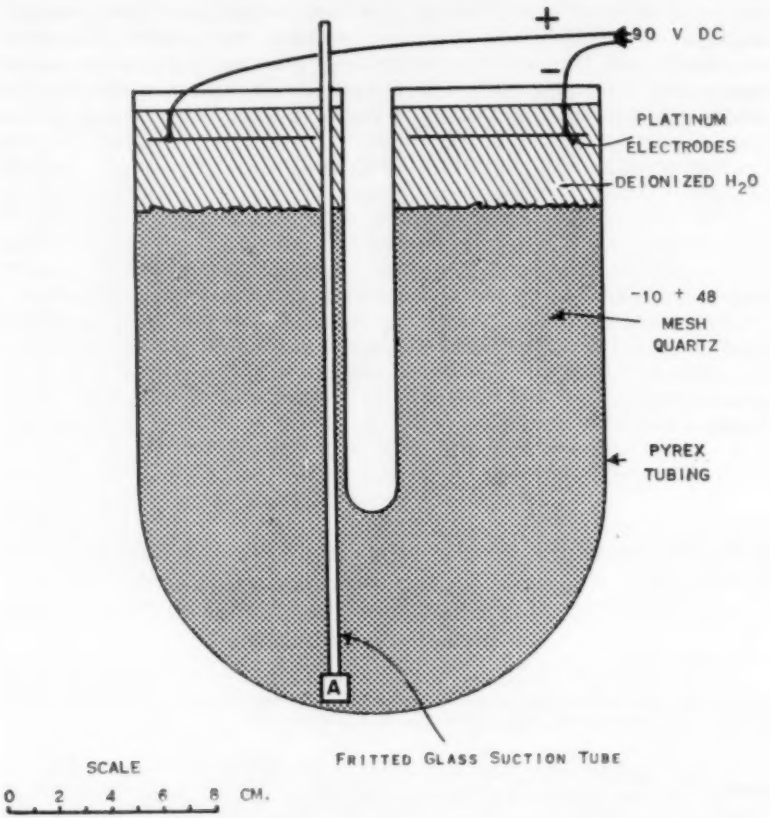

FIGURE 3. ELECTROLYTIC CLEANING CELL FOR REMOVING SURFACE IONS.

quartz grains is removed by applying suction to the fritted glass filter tube A. New deionized water is added and the process repeated until the current flow is constant at 0.08 ma, which is essentially the conductivity of the deionized water itself, corrected for the apparent decrease in cross section of the tube due to the presence of the quartz grains. It is then considered safe to assume that the quartz is clean and free from any ionizable impurities except those

within completely closed and sealed fluid-filled inclusions. In an experiment to verify this conclusion it was found that 100 mg of NaCl, added to a previously cleaned quartz sample, could be completely removed in several days, with three or four water changes.

In treating chert samples from limestones or dolomites, it was impossible to remove all of the carbonates, even with long digestion with hot acid. During electrolytic cleaning, these carbonate impurities caused a comparatively high current flow, and also caused the growth of small sharp rhombohedrons of calcite at the cathode, presumably by the reaction of the electrolytically transported Ca^{++} ions with CO_2 from the air. Under such circumstances it would be practically impossible to continue the electrolytic cleaning process long enough to have the current flow decrease to 0.08 ma.

Ball Milling.—The clean, −10 +48 mesh quartz grains, containing completely sealed fluid-filled inclusions, must be broken open to free the fluid from the inclusions. Either the surrounding quartz must be broken by externally applied forces, as by grinding in a ball mill, or it must be broken by internal forces, developed in the inclusion by heat or cold. The use of heat to decrepitate the inclusions is discussed beyond under the heading "Other Techniques." Repeated cycling from +290 to −29° C was found to be ineffectual for opening these tiny inclusions. In the ball milling procedure a 1 kg sample is run for 24 hours [8] in an alumina ball mill, using alumina grinding media with sufficient deionized water (approximately 400 ml) to insure a thin slurry of quartz and water as the final product. This procedure reduces practically all the quartz to grains 4μ and smaller, so that very few inclusions remain unopened. In some of the earlier work ordinary hard poreclain laboratory ball mills were used, with alumina grinding media,[9] but this method resulted in a higher blank. The slurry is separated from the balls with a stainless steel screen.

Separation of Soluble Materials from the Slurry of Quartz and Water.—The purpose here is to remove quantitatively, for analysis, the few tens or hundreds of milligrams of soluble salts contributed by the inclusion fluids, from the liter of slurry of finely ground, partially colloidal quartz and water.

In the early stages of the work filtration was used, but as a part of the quartz is colloidal in size, all filtration procedures yielded milky white filtrates, even after extended centrifuging. This milkiness was removed by forming a flocculent ferric hydroxide precipitate from added ferric nitrate. There are many difficulties inherent in this procedure, however, particularly that of keeping background or "blank" ion concentrations low when using such large volumes of solutions and reagents and such involved manipulations; in addition, there is a serious possibility of loss of inclusion materials by adsorption on either the large amount of quartz surface involved (estimated at 10^7 cm^2), or on the ferric hydroxide precipitate. These adsorptions could be expected to affect the ratios between various ions, as well as the total quantity of ions,

[8] It is felt that in future work this grinding time can be drastically reduced. Although the shorter time will leave more inclusions unopened, there are a number of obvious advantages that should more than compensate for the disadvantage of lower yield of inclusion fluids.

[9] "Burundum" grinding media were used (United States Stoneware Company). These media will chip the edges of most standard laboratory mills unless precautions are taken, such as decreasing the mill rpm or increasing the quantity of water used.

as surface adsorption is a function of both the concentration and the nature of the ions involved. The losses by adsorption on the quartz were minimized by the addition of a quadrivalent ion (Ce^{+4}) to displace the univalent alkali ions, and the losses by adsorption on the ferric hydroxide precipitate were minimized by performing a second precipitation of the iron after dissolving the original precipitate in HNO_3. However, as high blanks were obtained, all runs using this technique have been discarded and will not be reported here.

As a consequence of these and other difficulties, an entirely different method was developed, involving a separation of the ions from the quartz-water slurry. This procedure, making use of electrodialysis, proved very effective, and all compositional data reported here were obtained with it. There is a considerable volume of data in the literature on colloids on the design and operation of electrodialysis cells, but the cells are principally used for obtaining colloidal materials free of ionizable impurities, and hence generally are not designed to permit quantitative collection of the removed ions; many are designed to have a flow of distilled water in the electrode chambers to hasten the extraction, which makes them unsuitable for this particular application.

The cells that were used in work reported here were made of 3 rings, each approximately 6 cm long, of 15 cm (6 inch) diameter "Pyrex" tubing, and two "Pyrex" end plates, held together by tie rods through wooden pressure plates at the ends, as illustrated in Figure 4. An access hole was bored in the wall of each section. The basic principle is the use of an electric potential to drive the ions out of the quartz-water slurry in the center compartment, through the semipermeable membranes (M) and into the electrode chambers. The potential is applied to platinum gauze electrodes 6 inches in diameter and must be sufficiently high to overwhelm the opposing forces of diffusion, which attempt to equalize the concentrations throughout the three compartments. Eventually equilibrium will be established with a certain relatively high concentration of ions in the electrode chambers and another much lower concentration in the center compartment. The attainment of this condition of equilibrium is evidenced by a constant value of the amperage flowing at constant voltage; when this condition is attained the water in the electrode chambers is changed, as in the electrolytic cleaning cell. In all the experiments a potential of 90 volts direct current was maintained across the electrodes. Higher voltages would be desirable to speed up the migration of ions, hastening attainment of equilibrium, and to drive equilibrium further in the desired direction, but unfortunately they would also cause such undesirable effects as excessive heating and evolution of gas at the electrodes. Stirring might aid the extraction, but was not used as it would have been experimentally awkward. On the basis of synthetic blank runs, an arbitrary goal of 95 percent recovery of ions without serious alteration of ionic ratios appears feasible, by using 90 volts for two to three days, and two changes of water in the electrode chambers during that time.

A considerable number of experiments have been performed on the operation of the cells, as there are many unknown factors that must be evaluated empirically. Cell operation is such that membrane requirements are critical.

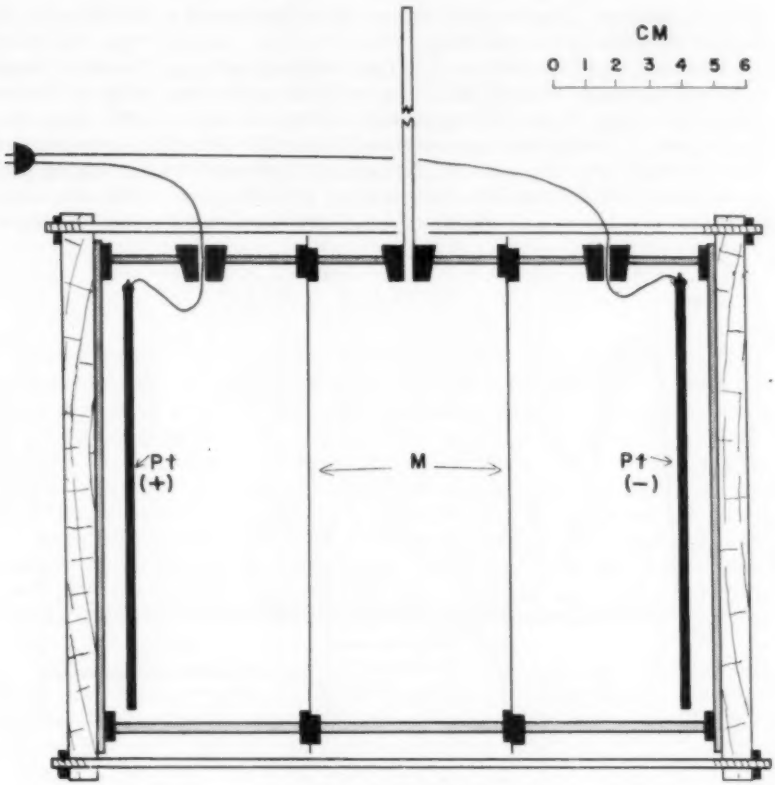

FIG. 4. Electrodialysis cell. The axis of the 15 cm "Pyrex" tubing lies horizontally, in the plane of the paper. The ground sample slurry is placed in the center compartment between the membrances, M, and deionized water is placed in the end compartments bearing the platinum gauze electrodes. The tube in the center compartment (40 cm long) permits an increase in volume in the center compartment by osmosis without bursting the membranes.

The membrane must be relatively low in electrical resistance, it must be sufficiently strong physically to stand the pressure exerted by a considerable head of water during water changes, it must have negligible ionic impurities, it must have pores adequate to permit the passage of ions as large as $SO_4^=$ yet not large enough to permit colloidal silica to penetrate, and it must be available in sheets large enough for the cell size chosen (6-inch-diameter circle).[10] In addition, it must be uniform in properties within one sheet and from one

[10] The overall dimensions of the cell are predicated by the volume of the quartz slurry (approximately 1,000 ml per run).

sheet to another. Various membranes have been tried and Visking's "R Zephyr" [11] seems to be most suitable.[12]

A record is kept of the amperage (at constant voltage), plotted vs. time, to provide a fairly reliable indication of ionic migrations. Figure 5 is a diagram showing the general appearance of these curves, in which time zero is the time of placing in the center compartment 1,000 ml of quartz-water slurry containing approximately 1,000 grams of minus 0.004 mm quartz, 400 ml of water, and 100 to 300 milligrams of ionizable salts. Within a comparatively few hours ions migrate through the membranes toward their re-

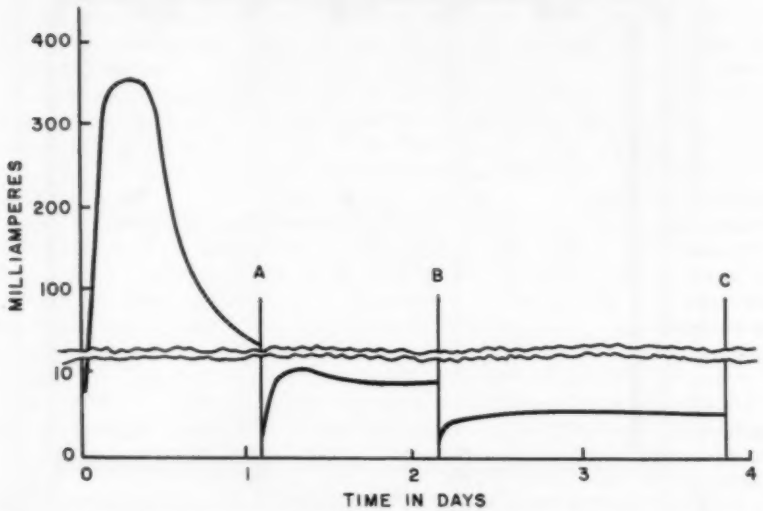

FIG. 5. Typical electrodialysis cell current flow (diagrammatic). The vertical lines at A, B, and C represent the times at which the solutions in the electrode chambers are removed and replaced with deionized water.

spective electrodes and greatly increase the conductivity of the previously deionized, low-conductivity water in these electrode compartments. The center compartment is rapidly depleted of ions and hence increases in resistance until its effects exceed those of the electrode chamber solutions and the current falls off rapidly, approaching the equilibrium value asymptotically. At this stage, back diffusion into the center compartment is occurring at a rate equal to migration out of the center compartment owing to the potential applied, and in order to permit further extraction from the center cell the water in the

[11] This seamless, regenerated, viscose process cellulose tubing was obtained from the Visking Corporation, 65th St. and Oak Park Ave., Chicago, Ill.

[12] Porous, etched but unsintered Vycor glass disks, 2 mm in thickness, were also tried as membranes, but did not permit extraction of more than approximately 75 percent of the ions in a synthetic blank in 20 days of operation. The glass was furnished through the courtesy of Dr. M. E. Nordberg of Corning Glass Company, Corning, N. Y.

electrode chambers is withdrawn by suction and replaced with new water. Immediately after the new ion-free water is placed in the end cells, the migration of ions once again takes place and the amperage curve goes through another maximum but at a much lower value, as 80 to 90 percent of the ions causing the conductivity is usually removed with the first change of water. A second change of water, after equilibrium is again approximately established, removes most of the remaining ions, and further changes after operation for four or five more days yield only small amounts of ions. A typical series of chloride analyses on the anode solutions follow:

	mg chlorine
Solution A (first water change)	24.9
Solution B (second water change)	4.1
Solution C (third water change)	1.2

Under most circumstances the minimum current flow at equilibrium lies between 5 and 10 ma, and when this current flow is reached but not exceeded after a change of water, it can be safely assumed that the ions present have been removed quantitatively, or essentially so, from the center cell. This condition usually occurs within 4 or 5 days of operation. As in the electrolytic cleaning operation, the presence of soluble minerals such as calcite in the slurry will not permit the amperage to drop until they are completely removed, and hence samples such as chert, containing calcite, were electrodialyzed only until they appeared to reach a temporary equilibrium at 30 ma (after 7 to 9 days), probably representing a constant rate of solution, and removal of solid calcium carbonate. It was assumed that the ions from the inclusions had been removed by this time.

Analysis.—The combined anode solutions are made alkaline to methyl red (in alcoholic solution) with NaOH to avoid loss of volatile acids [13] and then are evaporated to small volume. Sulfate is determined by precipitation and weighing as $BaSO_4$, and chloride (plus possible traces of bromide and iodide) as AgCl. No attempt has been made to determine $CO_3^=$, as a quantitative analysis for it would have no significance unless the whole operation were done in a CO_2-free atmosphere, with adequate provision for trapping gaseous CO_2 during the ball milling and at the anode during the electrodialysis. Even with these precautions there is the possibility of an unknown amount of CO_2 being formed in the electrodialysis operation by reaction of free oxygen, from the electrode, with the rubber gaskets and organic (cellulose) membranes.

The combined cathode solutions are evaporated to small volume, Ca^{++} removed as oxalate, and the alkali ions Li^+, Na^+, K^+, Rb^+, and Cs^+ determined by flame photometry with a Beckman model DU quartz spectrophotometer, using calibration curves prepared from synthetic mixed standard solutions approximating closely the chemical makeup of the unknowns. Li^+, Rb^+, and Cs^+ are run on a solution obtained by diluting the total cathode solution to 100 ml. Na^+ and K^+ are run on diluted aliquots of this 100 ml solution, so

[13] The first anode solution from a given run (hence containing the bulk of the anions) usually has a pH of about 5.

as to obtain concentrations in the most sensitive range for the instrument (approximately 20–40 ppm). The experimental procedure is such that there would be considerable ambiguity in any analysis for Ca^{++} or Mg^{++} (see beyond) and hence they are not determined.

After determination of the alkalies, the remaining solutions from several of the runs were evaporated to dryness, mixed with pure carbon, and analyzed spectrographically. Major amounts of sodium and potassium, and minor amounts of lithium, rubidium, and cesium were found. In addition, a number of other elements were found in trace amounts, but as these same elements were present in the blank runs, in the same ranges, the analyses are of little significance.

SOURCES OF CONTAMINATION AND ERROR

Other Minerals

It is obvious that any mineral impurities in the quartz that will yield any of the analyzed ions upon electrodialysis of the fine powder should be avoided. In the analysis of the alkali metals, feldspar, mica, and clay are perhaps the most serious contaminants. Potassium feldspar will react rapidly with pure water to yield solutions of rather high pH (R. M. Garrels, Harvard University, personal communication). It has been calculated that 125 grams of potassium feldspar in the quartz sample would yield only 100 mg of K^+ to the solution upon first contact. How much more K^+ might be obtained on electrodialysis of feldspar contaminants ground up with the quartz is difficult to say, but if the feldspar is completely decomposed during electrodialysis, 100 mg of K^+ would be obtained from 0.7 gram of feldspar. Micas are known to be decomposed by electrodialysis, leaving behind a silica-rich residue that yields a vaguely mica-like X-ray pattern (51); clays are particularly susceptible to decomposition, although fortunately they do not contain as high concentrations of the alkali metals as do feldspar and mica. It is common to find small amounts of these three minerals imbedded in quartz, and their recognition is not easy, particularly when they occur as submicroscopic "dust" inclusions in chert. If the amount is small, the effect on bulk grain density may be counterbalanced by the amount of fluid inclusions in the grains, and thus they would not be separable by density methods. As shown above, albite-rich plagioclase is not separable by the methods used, and would add Na^+ and Ca^{++} on electrodialysis.

Carbonates are particularly common with quartz, and small amounts of calcite, completely enclosed in quartz, may frequently be found even in acid-treated, −10 +48 mesh quartz. Although these carbonates will not yield alkali or chloride ions upon electrodialysis, their presence would slow down the electrodialysis operation, and would of course cause ambiguity in any determination of Ca^{++}, Mg^{++}, or $CO_3^{=}$.[14]

Sulfide minerals that may have escaped leaching, or free sulfur from the

[14] Each cubic millimeter of calcite, although it represents less than 3 ppm "impurity" in a kilogram of quartz, will yield approximately 1.1 mg of Ca^{++} and 1.6 mg of $CO_3^{=}$ on electrodialysis. There is adequate evidence, however, that the fluid in inclusions actually can contain large concentrations of calcium; see, for example, Zakharchénko (68).

leaching of sulfides with HNO_3 during sample preparation, might yield sulfate ion by oxidation at the anode, and soluble sulfates in the sample can be expected to yield sulfate ion readily on electrodialysis. Any relatively soluble mineral such as gypsum will be removed during the electrolytic cleaning unless it is completely enclosed by the quartz. It is possible that some of the ions removed during the cleaning operation result from the solution of substances such as secondary gypsum embedded in cracks in the quartz.

Adsorbed Ions

The original samples of one kilogram of −10 +48 mesh quartz consist of irregularly shaped grains having a total calculated surface area of approximately 5×10^4 cm^2; ball milling increases this surface area to approximately 10^7 cm^2 (28, p. 31). Gaudin, Spedden, and Laxen (27) found by radioactive tracer techniques that at a pH between 6 and 10, the adsorption of the Na^+ ion on quartz surfaces, from a solution containing 10^{-2} to 10^{-3} moles Na^+ per liter, was approximately 10^{-10} moles Na^+ per square centimeter of quartz surface. At low concentrations adsorption on quartz is found to vary directly as the square root of the solution concentration (26). As these experiments represent a close approximation to the conditions in the slurry at the end of the ball milling, they indicate that an appreciable portion (∽ one millimole, 23 milligrams) of the Na^+ from the inclusions could be adsorbed onto the quartz surface. Gaudin, Spedden, and Laxen (27) also show that K^+ will displace the Na^+, so it is obvious that adsorption cannot be ignored in the final slurry, although it can only account for insignificant amounts of ions (approximately 0.1 mg) on the surfaces of the original −10 +48 mesh sample.[15] It is felt, however, on the basis of a study of a series of synthetic blanks, that electrodialysis is capable of pulling these ions off these surfaces, presumably by replacing them with hydrogen ions or oriented H_2O dipoles.

In order to check on the possibility that the hydrochloric acid used in leaching is the source of the chloride found, duplicate runs were made on two splits of a sample, one leached with HCl and one with HNO_3 (see under "Results Obtained"). These showed that the acid used did not affect the chloride analysis.

Foreign Ions in the Structure

It is well known that natural quartz is not "pure" SiO_2. A variety of elements are found in it upon spectrographic analysis, although some of the samples analyzed probably contained fluid inclusions that contributed at least a portion of the trace elements such as Li, Na, and Ca[16] that are found (37, p. 242; 24, p. 1216). Some of the best analytical work on foreign ions in quartz has been done on sawn slabs from oscillator-grade (and hence inclusion-

[15] It is possible that some of the ions removed in the cleaning operation come from adsorption on lineage surfaces (8) within the individual −10 +48 mesh grains. St. Clair (58) found that abnormally high absorption of H_2S gas on coarse galena grains, per unit of apparent surface area, disappeared when the size was reduced to a "fraction of a millimeter," and hence was probably related to the extra surface provided by the lineage cracks.

[16] Even one inclusion of 1 mm^3 volume, in a 1 cm^3 sample of quartz, would result in 37 ppm Na in the sample if the inclusion fluid contained 10 percent Na.

free) quartz. The amounts of certain foreign ions found in several studies on natural quartz samples are given in Table 1. From this table it is evident that there are small but significant amounts of Li^+, Na^+, and K^+ in the quartz structure, and in rare instances these may be considerably higher. Even the purest natural quartz (analysis 3, Table 1) contains one impurity atom for every 5,000 silicon atoms; in this sample 90 percent of the impurity atoms are lithium.

These foreign ions in quartz present several problems. A large amount of quartz surface is exposed on ball milling (10^7 cm²/kilogram sample); if

TABLE 1

RANGE OF CERTAIN ELEMENTS IN NATURAL QUARTZ, IN PERCENT—FROM SEVERAL AUTHORS *

	1		2		3	4		5	
	Min.	Max.	Min.	Max.		Min.	Max.	Min.	Max.
Al	0.005	≫0.01	0.000X	0.01	0.0004	—		0.0000	0.0002
Fe	0.001	>0.01	0.00X		0.0000	—		0.0000	0.014
Mg	<0.0005	~0.01	0.000X	0.001–0.01	—	—		—	
Ca	>0.0005	~0.01	0.00X		—	—		—	
Li	0.0003		NF	0.01–0.1	0.002	0.00005	0.0038	0.0002	0.0017
Na	0.003		0.0001–0.0005	0.001–0.03	0.0003	—		0.0000	0.0008
K	NF		NF	0.0005–0.005	0.0002	—		0.0000	0.0008
Rb	NF		NF		—	—		—	
Cs	—		NF		—	—		—	

* Note: "Min." and "Max." refer usually to different samples. As there are differences in sensitivity and method of presentation of spectrographic data by different authors, these data are not all strictly comparable. Other elements were determined but are not reported here. To convert these data to milligrams per 1,000 gram sample (= ppm), so that they may be compared with the fluid inclusion data, multiply the percentage by 10^4; thus 0.0003 percent Li means 3 milligrams of Li would be present in the sample. NF—Not found; X—a number between 1 and 9.

1. Cohen and Sumner (14).

2. Keith and Tuttle (37). Limit of detectability for Li, Na, and K is 0.0001 percent, for Rb and Cs, 0.0003 percent. The high values for Li, Na, and K are for a single sample of pale green color from Iceland that showed a very low inversion temperature (536° C).

3. Frondel and Hurlbut (24). An exceptionally pure Hot Springs, Ark., crystal, used for silicon atomic weight determinations. Analysis by wet chemical methods with flame photometer determinations of the alkalies. Results originally presented as oxides.

4. Horstman (32), p. 9.

5. Frondel and Hurlbut (25). Wet chemical analyses with flame photometer determination of the alkalies. Inclusion-free material, except a rose quartz which gave the high values for Li and Na, and contained rutile inclusions. Results originally presented as oxides.

these ions, particularly the alkalies, are released from the quartz structure during the run, they could not be distinguished from the ions coming from the fluid inclusions. Simple leaching from the exposed surface is inadequate to provide significant amounts of contamination to the solution, unless some mechanism is invoked that will also contribute ions from the *interior* of the grains.

Unfortunately, a possible mechanism is provided by the unexpectedly high electrical conductivity of quartz along the *c* direction. This high conductivity was first shown, in 1886, by Curie (16), and detailed experiments on the

phenomenon were described in 1888 by Warburg and Tegetmeier (65). In 1925 Bragg and Gibbs (4) explained it on the basis of the crystal structure of quartz. They proved that it results from the movement of small cations such as Na^+ and Li^+ along the large channels they had found to exist parallel to the *c* axis in the structure. Joffe (35) describes the actual "cleaning" of the foreign ions out of natural quartz by applying an electric field, and if an alkali-rich anode is used, alkali ions can be pushed through the structure (30, 62). Most of this work has been done at elevated temperatures and high voltages, for example Hammond, Chi, and Stanley (29), used 3,000 volts across 6 mm of quartz at 530° C.

It is difficult to apply these results here, particularly as the conductivity of quartz and the rate of movement of ions in it decrease so rapidly with a drop in temperature. However, a crude but conservative calculation indicates this source of contamination during electrodialysis is negligible. In this calculation it was assumed that half the quartz grains in the electrodialysis cell were oriented with *c* parallel with the current flow, and that the sample was in an electric field of 5 volts per centimeter, at approximately 30° C, for four days. It was further assumed that these oriented grains had a constant resistivity of 0.5×10^{14} ohms per cm^2 per cm (interpolated from data given by Sosman, 57, p. 528), that *all* the current flow in the quartz grains was by movement of lithium ions, and that Ohm's law held. The calculation showed that under these conditions the amount of lithium that would be moved out of the quartz structure and hence contributed as contamination to the electrodialysis cell would be only 1×10^{-3} milligrams per run. This probably represents a maximum possible movement, as the assumptions on which the calculation is based are conservative.[16a]

Sodium, although it is present in larger amounts in quartz than is lithium, is too large for the channels (9) and hence does not move as rapidly as lithium (62). In addition, sodium is present in such comparatively large amounts in the fluid inclusions that any error introduced by contributions from the structure would be small.

Ball Milling

This step of the process obviously must introduce some impurities, and yet it is practically impossible to set up a truly rigorous "blank" run to estimate the magnitude of this variable, owing to the necessity of deviating from the established procedure during the blank run. On grinding a normal sample of quartz for 24 hours, approximately 42 grams of material insoluble in $HF\text{-}H_2SO_4$ is left in the sample, representing abrasion from the ball mill and grinding media. This is essentially pure Al_2O_3, as the residue from the quartz itself, as shown by Table 1, amounts to several orders of magnitude less than this 42 grams per sample. A six-hour blank run with the normal charge of grinding media and deionized water in an empty alumina mill yielded 125.2 grams of powdered mill + media, indicating an abrasion rate nearly

[16a] There is probably some conductance from the movement of holes, electrons, and ions other than lithium (62), the resistance may increase with time in the cell, and lithium ions may not be able to move at all in this low an electrical field.

12 times that obtained when a quartz sample was present. On electrodialysis this slurry yielded the following amounts of ions, in milligrams: Na^+ 18; K^+ 22; Cl^- 5.9; $SO_4^=$ 4.6. In all the reported data the HF-H_2SO_4 insoluble residue has been determined analytically for each sample run and an approximate correction based on the above analysis has been made for ions from this source. Thus if 42 grams of HF-H_2SO_4 insoluble residue are found in a run, the following milligrams of ions are assumed to be from the mill and grinding media: Na^+ 5; K^+ 7; Cl^- 2; $SO_4^=$ 1. Although varying with the nature of the sample, this correction is usually less than 10 percent of the total amounts of Na^+, K^+, and Cl^- present.

The experiment reported above does not represent a true blank in that the conditions of grinding are not identical with a normal run. Actually, it is not possible to design a true blank run, unless a kilogram of pure quartz could be obtained, free from fluid inclusions and free from impurities within the structure, and preferably another kilogram, also free from impurities within the structure, but containing known amounts of inclusions of known composition. Attempts to approach the first ideal, by using inclusion-free scraps from quartz oscillator cutting operations, are under way. Unfortunately for this work, synthetic quartz crystals, grown from known fluids, have too few inclusions even in the rejects to be used as the second ideal sample. Blanks run using samples of clean transparent fused silica cullet (General Electric Co.) in place of quartz showed anomalously high Na^+ and K^+ results. One possible interpretation of these high results would be that the fused glass, which ground much more readily and hence yielded a much finer product, contributed on electrodialysis all the impurities that had been in the original quartz from which the glass was made. Analyses of the unground glass indicate the presence of impurities in the right order of magnitude.

It seems likely that the possible contribution of $SO_4^=$ from sulfur in the rubber gaskets of the mills was negligible, as only the edge of the gasket was in contact with the slurry throughout the grinding period. The construction of the mills used is such that no abrasion of the gasket took place, and the possibility of contamination from sulfur deposits on the surface of the gasket was precluded by adequate cleaning before use.

Losses on Opening

There are two possibilities whereby the results obtained might be biased—that is, not representative of the true gross composition of the fluid inclusions in the sample. First, if *all* the inclusions in a given −10 +48 mesh sample are not opened in the ball milling, and the composition of the unopened inclusions is different from the opened ones, the analytical results would be biased. Examination of the ground samples in a number of runs indicated that only a very few exceedingly minute inclusions escape unopened, so the procedure for opening of the inclusions seems to be adequate to preclude any serious difficulties from this cause (see footnote 8).

A much more significant possibility for sample bias exists in the loss of inclusions upon crushing to −10 +48 mesh. A large part of the total amount

of inclusion fluids in a given sample may be present in a very few large inclusions. As shown by Figure 1, one inclusion of 1 mm diameter contains as much fluid as 10^9 inclusions 1μ in diameter. During crushing to -10 $+48$ mesh, most of these larger inclusions will be opened and their contents lost. If there are two sets of inclusions in the sample, one primary and the other secondary, it is common to find that the primary inclusions are much larger, on the average, than are the secondary inclusions; if the composition of the fluids in these two is different, the results obtained in the later ball milling will be biased accordingly. Even if there is no difference in size, if one set contains water-rich liquid and gas at less than one atmosphere vapor pressure, and the other set contains liquid CO_2 and gas at high pressures, crushing to -10 $+48$ mesh might well be expected to open preferentially many of the high-pressure, CO_2-filled inclusions and bias the sample.

Even if all the inclusions in a given sample were formed at the same time, there is some question whether the composition of the fluid trapped in the small inclusions would be the same as that trapped in the large ones. The well-known but poorly-understood fact that concentration gradients exist in the fluid at the surface of a growing crystal might provide a possible mechanism for such differences. Since the pioneer work of Miers (45) in which it was shown that a layer of supersaturated liquid existed at the growing surface of a crystal, there have been many studies of the concentration gradients around growing crystals. Although sizable concentration gradients have been found in the fluid at the surface of rapidly growing crystals, apparently extending out more than 100μ from the surface of some crystals (2, 10), most of this work has dealt with the high concentrations of a given water-soluble salt in saturated and supersaturated solutions from which crystals of that same salt were growing. Experiments reported by Miers (45), using total reflection phenomena, would require that at the immediate surface of the growing crystal, and for at least some hundreds of angstroms out into the fluid (7, p. 166), the concentration of the salt that is crystallizing would be *greater* than in the fluid as a whole.[17]

In trapping fluid in inclusions in natural quartz, we are not concerned as much with silica concentration gradients in the fluid near the growing surface as we are with concentration gradients of the other ions (Na^+, K^+, Cl^-, etc.) that seem to be universally present in natural fluid-filled inclusions. The saturated substance (silica) is presumably present in comparatively small concentrations, and so its crystallization should not be of much consequence in affecting the high concentrations of other ions in the fluid near the growing surface of the crystal.

One other possible cause of differences in the compositions of the fluids in large and small inclusions must be considered. The unsatisfied charges on a growing quartz crystal surface will affect the distribution of any ions in the fluid near it, but it is not known at what distance into the fluid these

[17] It is possible that these higher concentrations might be a result of the heat of crystallization released at the surface of the growing crystal. If this is true, it should be tested by similar studies on salts having retrograde solubility. Dreyer, Garrels, and Howland (21) proposed that the unexpectedly high temperatures of filling that they found for inclusions in salt might be explained by higher temperatures at the (rapidly) growing surface from the heat of crystallization.

charges can be expected to be effective. Unless the surface of the crystal has a large net charge, it seems unlikely that these unsatisfied charges can have more than a very local effect (i.e., 10 angstroms or less). As most of the fluid inclusions studied here are 1μ in diameter (10^4 angstroms) or larger, even large compositional differences between such thin surface layers of fluid and the bulk of the fluid would not be particularly significant in affecting the composition of the fluids trapped in the inclusions.

There is considerable evidence from numerous published heating-stage (and cooling-stage) studies that large and small inclusions of the same generation have the same ratio of liquid to gas, as well as the same thermal expansion coefficient and freezing point depression for the liquid. The logical assumption from this would be that the composition of the liquid was the same. These studies, however, have not included work on inclusions as small as 1μ in diameter, where metastability (e.g., failure to nucleate ice crystals) is difficult to avoid, and additional cooling-stage studies are being planned to verify this assumption.

In any case, it would appear desirable to use coarser material in the ball mill, giving a larger yield of inclusion fluid per kilogram, and less bias, if it can be done without seriously increasing the risk of contamination from extraneous substances.

Electrodialysis

Other than the possible removal of extraneous ions from the quartz structure proper, mentioned above, there are several other sources of error that must be evaluated. They arise from the addition of ions from the materials making up the electrodialysis cell, or the loss of ions by incomplete extraction in the electrodialysis.

Addition of Ions.—In this respect, all components of the cell must be viewed with suspicion until proven innocent. The platinum electrodes obviously will add nothing, if they are clean and pure. The other materials of the cell, however, "Pyrex," rubber, and membrane, each may contribute. In the cells there is exposed a total of 1,200 cm² of "Pyrex" surface.[18] One-third of this is in contact with a mildly alkaline (0.005 N), practically stationary solution (cathode compartment, during the early part of run) while another third is in contact with a similarly mild acid solution (anode compartment). In the latter parts of the runs, after the first water change, the glass surfaces are in contact with essentially pure water. The behavior of "Pyrex" in contact with various liquids under a variety of conditions has been the subject of many investigations, but none of these duplicates directly the conditions in the electrodialysis cell. Under a test devised for comparing the chemical durability of glass powders (11), which involves contact with 0.02 N H_2SO_4 at 90° C for 4 hours in a "Pyrex" erlenmeyer flask, the flask itself yielded 0.40 mg dissolved alkalies as Na_2O (1). If the entire 1,200 cm² of "Pyrex" surface in the cell lost alkali proportionately during the electrodialysis run, less than 10 mg would be obtained. The glass apparently "ages" rapidly on acid attack, however, as only 8 percent of the above amount of alkali was

[18] Presumably this is all Code No. 774 composition, "Pyrex chemical resistant glass."

dissolved in the fourth 4-hour run in the same flask (1).[19] The electrodialysis cells were first used for many weeks on blank runs, and were always operated for at least several days, cleaning membranes, before an actual run was put in, so presumably the glass surfaces were "aged" and the contributions from this source reduced accordingly.

Under treatment with alkaline solvents, however, "Pyrex" is not as resistant. Wichers, Finn, and Clabaugh (67) found that "N/20" NaOH solution, gently boiling for 6 hours, caused a total weight loss from the glass nearly 100 times as great, per unit of surface exposed, as the alkali loss found by Burch, described above. When this weight loss is converted to milligrams of alkali, however, assuming 4.2 percent $Na_2O + K_2O$ in "Pyrex," the leaching with this stronger alkaline solution is found to be only 4 times that with the acid. There is no apparent improvement in the chemical durability of various glass surfaces under continued treatment with alkaline solutions, however (13).

Although the above would indicate that the "Pyrex" walls of the cell can be expected to provide some alkali (particularly sodium) to the cathode solutions, the amounts involved, as determined by various blank runs, are not large compared with the quantities coming from the inclusions themselves. In the actual runs, this factor has been accounted for, at least partially, in the correction for the ball milling blank, which includes all electrodialysis contributions. It is planned to construct new cells of polyethylene to avoid this source of error completely.

The rubber stoppers and gaskets used in the cell were of "sulfur-free" grade, and were scoured carefully before use, so there is little likelihood of serious contamination from them. The membranes as originally received, however, contain considerable ionizable materials and must be cleaned by washing, followed by electrodialysis with the new membranes loose in the center cell; after this the new membranes are placed in position in the cell and a blank run for a day or more. Any contribution from the membranes after this treatment is negligible.

Loss of Ions.—As the extraction of ions from the slurry is not complete, there are possibilities of errors in the ratios of various ions if there are differences in the completeness of the extraction. It is known that there are significant differences in the rates of migration of various ions, so the ionic ratios in the electrode chambers will change with time. The size of the pores in the membranes appears to be the major controlling factor here; available information indicates an average pore diameter of only 50 angstroms in the hydrated Visking "R-Zephyr" membrane, and the unhydrated $SO_4^=$ ion is about 5 angstroms in diameter. If the water-swollen membrane is 0.1 mm thick, the shortest possible path for the $SO_4^=$ ion is a hole 10^6 angstroms long and only ten times as wide as the ion. As a result of this long path and because the composition of the solution is not necessarily similar from one run to the next, it is necessary to run the cell for a sufficient number of days and with a sufficient number of water changes so that essentially all ionizable materials are removed from the slurry. Considerable differences in the

[19] Similar "aging" is reported for other borosilicate glasses on treatment with plain water (13).

mobilities of the alkalies were noticed when the several cathode solutions from a given run were analyzed individually; as would be expected, Na^+ moved faster than K^+. (As an example, in the first change of water on a synthetic blank, made with a 1:1 weight ratio of Na^+/K^+, the ratio was 3:1.) It is felt, however, on the basis of various blank runs, made by introducing known amounts of ions into a quartz sample in the center cell, that at least 90 percent, and probably at least 95 percent, of the ions are extracted from the quartz slurry during a run, with little change in ratios.

Another possibility of error lies in the loss of volatile gases, particularly chlorine or hydrochloric acid, from the anode chamber. The exact ionic species present in the anode chamber during the electrodialysis of a sample are not known. As even the maximum concentrations are low, seldom exceeding 100 mg Cl^- per liter, and the electrode surfaces are large (6 inch circle of platinum gauze), loss by volatilization of either Cl_2 or HCl, along with the small amount of oxygen evolved, is not likely. Neither could be detected by odor in the gases at the top of the anode compartment, and if the losses were significant, they should have been apparent in the analyses of the blank runs.

Analysis and Reagents

In the early chemical separation procedure used in this study, involving elaborate chemical manipulations as described above, contamination from the reagents, glassware, water, and other sources was very serious. In the later work using electrodialysis, however, the impurities introduced from these sources, such as the precipitants used in the analytical work, could be proven to be negligible. The only reagent used in any quantity is water, and as it was purified by passing distilled water through a mixed-bed resin deionizer, it contained very little extraneous material.[20] As "Pyrex" rather than polyethylene vessels were used in this work, much of the sodium found in the various types of blanks run (mostly amounting to only a few milligrams) could be attributed to this source.

The analytical determinations of sodium and potassium probably have smaller errors than the other alkali determinations—in percent of the total amount found—as considerable time was spent in developing mixed standards that would approach closely the composition of the unknowns in the flame photometer analysis. The errors from this source are certainly smaller in magnitude than those introduced from the other sources in the procedure. The flame photometer analysis of a given solution could be reproduced within ± 2 percent of the determined Na^+ or K^+.

No great accuracy can be claimed for the determinations of the rarer alkali metals, Li, Rb, and Cs, as the amounts found, although significant in most samples (>0.1 mg), were closer to the limit of detection with the method

[20] At one time the resin in the demineralizer apparently deteriorated, and yielded small amounts of organic matter in the deionized water. Although this water still had a high resistance and few ions, the organic matter apparently influences the flame photometer emission characteristics significantly and these runs had to be reanalyzed after destruction of the organic matter.

used. The figures given in the second decimal place (0.0X) probably have no real significance.

The method of determining chloride is comparatively easy and gave no difficulty, hence the errors in the chloride analyses are probably small, if the Br and I content is low. If small amounts of ClO^- or other similar ions occur in the anode solutions, they might cause low results in analysis for total chlorine as chloride. In view of the conditions used, however, it seems unlikely that chlorine-bearing ions other than Cl^- occur in the anode solutions. Even if they were present, it is reasonable to expect that they would be reduced to Cl^- during the evaporation of the anode solutions to small volume, as an organic indicator in alcohol solution is present, having been added earlier during the pH adjustment.

The determinations of the sulfate ion are probably not very significant. This lack of significance arises, not from shortcomings of the analytical procedure, but from possible oxidation of sulfur or sulfides during the ball milling or electrodialysis. If H_2S is present in the inclusions (a rare occurrence), it might also be converted to $SO_4^=$.

RESULTS OBTAINED

Before stating the results, it should be emphasized that owing to the very nature of the process, absolute amounts of salts, per kilogram of quartz, would be of comparatively little value. The quartz from any one occurrence will vary tremendously in the *amount* of liquid present in inclusions; we are mainly interested in the relative ratios of the ions in this liquid. The problem of incomplete extraction also makes any statement of the absolute amounts of salts per kilogram of quartz hazardous, so until some method can be developed whereby the total volume of inclusion liquid extracted can be measured, as well as the weight of salts, interpretation of the analytical work should be based mainly on the ratios between ions. However, the actual milligrams of salts found per kilogram of quartz will be given for evaluation of the potential usefulness of the method.

Series 1.—In the beginning of the investigation, a series of samples representing a variety of geologic occurrences and textural types of quartz were run, in order to learn more concerning the experimental technique, the possible range of values that might be obtained, and the limitations of the method. The results on this series of runs are summarized in Table 2. A considerable amount of data obtained earlier by the iron hydroxide-coagulation technique is substantially in agreement with the data of Table 2, but is not directly comparable owing to the limitations of that method, as described. It should be noted that more than one run was made on samples 16 and 23; 3 runs, *a*, *b*, and *c*, were made on sample 16, one pair (16*a* and 16*b*) to check on the possibility of contamination from the leaching acid, and another pair (16*b* and 16*c*) to check on duplicability of results using essentially identical techniques except for minor differences in grinding time, etc. The two runs on sample 23 were made as a check on duplicability.

Lithium and rubilium concentrations were comparatively low in these

TABLE 2

SERIES 1. PARTIAL ANALYSES OF IONS IN FLUID-FILLED INCLUSIONS IN QUARTZ FROM SEVERAL DIFFERENT ENVIRONMENTS

Sample run	Cleaning acid used	Milligrams found in the fluids from the fluid-filled inclusions in 1 kg of quartz							Ratios					
									Weight			Atomic and molecular		
		Na^+	K^+	Li^+	Rb^+	Cs^+	Cl^-	$SO_4^{=}$*	Na/K	Li/Rb	Cl/SO_4	Na/K	Li/Rb	Cl/SO_4
"A"	HCl	85	100	1.85	0.21	0.1	27	6	0.85	9.	4.5	1.44	110	12.
9	HCl	32	30	0.1 ±	0.1 ±	<0.1	29	22	1.07	?	1.3	1.82	?	3.5
16*a*	HNO_3	130	90	1.45	0.1 ±	<0.1	50	5	1.44	14.	10.	2.45	170	27.
16*b*	HCl	107	75	0.95	0.1 ±	<0.1	41	6	1.43	9.	7.	2.43	110	19.
16*c*	HCl	110	80	0.83	0.1 ±	<0.1	31	5	1.37	8.	6.	2.33	100	16.
23*a*	HCl	85	445	0.70	1.23	0.2	120	140	0.19	0.6	0.86	0.32	7	2.3
23*b*	HCl	85	440	0.62	1.22	0.15	117	139	0.19	0.5	0.84	0.32	6	2.3
26	HNO_3	125	155	0.83	0.45	0.1	151	13	0.81	1.8	12.	1.38	22	33.

* Analysis subject to limitations—see text.

Notes on Samples

Sample	Locality	Geologic occurrence	Associated minerals in sample, before mineral separation
"A"	North end of the Quitman Mts., eight miles due west of Sierra Blanca, Texas.	White euhedral quartz crystals embedded in platy specularite of "high temperature" quartz-garnet-hematite contact metamorphic zone between Cretaceous sediments and Tertiary (?) intrusive body. Perhaps 50 percent of the inclusions are "primary."	Hematite (most of the crystals had weathered free).
9	Maxfield mine, Little Cottonwood Canyon, 16 miles southeast of Salt Lake City, Utah.	White euhedral quartz crystals in vugs in mesothermal replacement vein. Perhaps 50 percent of the inclusions are "primary." Mutual crystal growth interference proved that some (and probably most) of these crystals formed simultaneously with pyrite crystals.	Considerable pyrite, galena, and sphalerite.
16	Farmington Canyon, 1.95 miles northeast of Farmington, Utah. Roadcut just below stream-gaging station.	Grayish quartz-rich center of small (3 feet thick) cross cutting pod-like pegmatite in hornblende schist. Edges of pod contained considerable feldspar and biotite. Criteria for primary vs. secondary inclusions inapplicable.	Small amounts of feldspar, mica, chlorite, and pyrite.
23	Provo Canyon, Utah. Roadcut just below Deer Creek Dam.	Apparently "primary" dark gray fine-grained chert nodules in late Paleozoic limestone. Inclusions of unknown origin.	Abundant carbonates.
26	Southeast side of Antelope Island, Great Salt Lake, Utah; 0.8 mile north of west end of dike connecting island with mainland.	Three foot massive white quartz pod in chlorite schist. Criteria for primary vs. secondary inclusions inapplicable.	Thin stringers of chlorite and isolated pyrite cubes.

samples, but there are significant differences in some of the Li/Rb ratios in different specimens. The variation in Li/Rb ratio for the three runs on No. 16 is expectable because the Rb^+ content was at the lower limit for the flame photometer technique used in this case. Lithium was very high, relative to other alkalies, in sample "A." Cesium concentrations, except in the chert (No. 23), are all at the lower limit of the flame photometer sensitivity and the determinations are of minor value, except to indicate that there has been very little concentration of Cs^+ relative to Na^+ in the formation of these liquids. Geochemical evidence indicates that in at least some samples the Cs^+ concentration should be considerably greater. If inclusions contained the same Na/Cs ratio as rocks, approximately 0.03 mg Cs^+ should be present, along with 140 mg of Na^+, if there is no enrichment, and the large size of the Cs^+ ion should make 10-fold enrichments occur commonly.[21]

In order to evaluate these results, the ratios of elements in the inclusions may be compared with the ratios for ordinary rocks. If the ratios are the same in rocks and inclusions, the abundance ratios of Na/Rb and Na/Li in the crust of the earth indicate that inclusion liquids in quartz showing 140 mg Na^+ should also contain 1.4 mg Rb^+ and 0.2 mg Li^+. The results obtained (Table 2) show the average Rb^+ is well below, and the average Li^+ is five to ten times more than the above values. Geochemically this difference is to be expected, as crystallization of potassium minerals will trap Rb^+, but the small size of the Li^+ ion should cause it to become highly enriched in late fluids, as evidenced by the lithium pegmatites, if it is not trapped in Mg^{++} sites during the growth of magnesium minerals.

Most important from the standpoint of possible correlations of epochs of quartz deposition are the amounts of Na^+ and K^+. As these ions are present in considerably larger amounts than the other alkalies, their extraction and determination is subject to less error. Once again, the three different runs on sample no. 16, using slightly different techniques, all gave a Na/K ratio of 1.41 ± 0.04, although the actual quantities found varied as much as 20 percent. Presumably this variation is a result of variation in the efficiency of extraction. The very low Na/K ratio in the chert (a reflection of a very high K^+ value) and its high Rb^+ value, cannot be interpreted satisfactorily at this time. One percent of a potassium-bearing clay mineral would be very difficult to recognize, and yet could easily yield, upon electrodialysis, both the K^+ and Rb^+ found.[22] It is possible, however, that fluid inclusions could have such compositions. The agreement between the analyses for the two runs on sample 23 is considered to be completely fortuitous, in view of the known experimental errors affecting duplicability. It is a striking example of what is probably a combination of compensating errors and coincidence.

The Cl/SO_4 ratios in Table 2 show considerably more variation than that expected from the technique itself, unless undetected sulfides were present in some of the samples and yielded sulfate ion on ball milling or electrodialysis.

[21] Horstman (32) lists the K/Rb ratio in igneous rocks as 270, and the K/Cs ratio as 7,000.

[22] Maxwell (44) reports analyses of 24 cherts, of which 5 show much higher K_2O than the remaining 19 (0.10 to 0.33 percent, compared with 0.00 to 0.05 percent). Two of these same 5 samples had the highest Li^+ values obtained (32 and 36 ppm), and the other 3 averaged twice as high in Li^+ content as the remainder.

None of the samples yielded detectable H_2S on crushing or ball milling. The interpretation of these anion analyses is difficult, as one of the most abundant anions known to be present in inclusions, carbonate, as HCO_3^- or $CO_3^=$, cannot be determined adequately with the electrodialysis technique used. It was hoped that the use of porous glass "membranes" made of etched but unsintered "Vycor" glass would permit such determinations, by avoiding the possibility of contamination by CO_2 from oxidation of the membranes, but this glass was not satisfactory, as mentioned above. It is obvious from Table 2 that the sum of $Cl^- + SO_4^=$ is far from adequate to balance the $Na^+ + K^+$ found; as much as several hundred milligrams of $CO_3^=$ would be needed to attain balance. It would be more satisfactory, of course, to be able to determine the CO_2 directly, so that anion/cation balances could be determined. Unless free CO_2 were present these balances might help to distinguish between ions yielded by the electrodialysis of possible contaminating clays (or foreign ions in the structure), and those from the inclusions themselves.

It would also be highly desirable to know the absolute concentrations in the inclusion fluids themselves. To obtain these from the data of Table 2, it is necessary to know the total volume of inclusion fluids. Estimates of the total volume of inclusions, made using optical measurements at high magnification on statistically significant samples of quartz, indicated that white quartz of the type used in this work contained approximately 0.1 percent liquid as inclusions. Thus, one kilogram of quartz would contain about one gram of liquid, and the data of Table 2 indicate that this fluid contains between 200 and 300 mg of salts in solution, or 20 to 30 percent by weight (approximately 4-molar). Although these data are very crude, they are in line with data obtained by others using the occasional large inclusions found in quartz, and with the known occurrence of solid alkali chloride crystals in the fluid of some inclusions.

It would also be desirable, of course, to have analyses for several other ionic constituents such as H^+(pH), e^-(Eh), F^-, Br^-, Be^{++}, $BO_3^{\equiv}$, and many others, but the experimental problems involved in these determinations are too severe at this time. The determination of $BO_3^{\equiv}$ would necessitate elimination of all "Pyrex" surfaces, as it is probable that more boron than sodium would be extracted from the surfaces of the "Pyrex" (personal communication, M. E. Nordberg, Corning Glass Works, October 1, 1957). A polyethylene electrodialysis cell is being designed for this purpose [23] and should also aid in reducing contamination with Na^+. The heavy metals should be determined, but contamination from numerous sources, particularly from ore mineral grains, practically precludes there being any significance to the determinations.

Series 2.—As the results of series 1 were encouraging, it was felt that a series of samples, all from the same mineral deposit, should be run. Quartz from gold-quartz veins was chosen, as most of the inclusions in such veins are known to be secondary,[24] i.e., the result of healing of numerous shears

[23] The borate anion has been found in fluid inclusions in quartz (63a; 67a, 67b).

[24] Ferguson and Gannett (23), noted two types of inclusions, primary and secondary, in the gold-quartz of the Allegheny district; the large numbers of secondary inclusions apparently contained no vapor bubbles.

TABLE 3

SERIES 2. PARTIAL ANALYSES OF IONS IN FLUID-FILLED INCLUSIONS IN QUARTZ FROM SIX GOLD-QUARTZ VEINS IN THE GRASS VALLEY DISTRICT, CALIFORNIA

Sample No.	Location	Milligrams found in the fluids from the fluid-filled inclusions in 1 kg of quartz							Ratios						Associated minerals in sample, before mineral separations
									Weight			Atomic and molecular			
		Na^+	K^+	Li^+	Rb^+	Cs^+	Cl^-	$SO_4^{=}$*	Na/K	Li/Rb	Cl/SO_4	Na/K	Li/Rb	Cl/SO_4	
44	North Star vein	100	105	0.72	0.68	0.32	97.0	34.9	0.95	1.1	2.8	1.62	13	7.6	Decomposed feldspar, chlorite.
45	Empire vein	100	100	1.2	0.45	<0.05	140.9	28.8	1.00	2.7	4.9	1.70	33	13.	Pyrite, chlorite, decomposed feldspar, native gold, gouge (unidentified).
46	No. 5 vein, North Star Mine	117	114	0.72	0.45	0.05	193.2	27.9	1.03	1.6	6.9	1.75	20	19.	Limonite, chlorite, pyrite, galena, gouge (unidentified).
47	No. 2 vein, Empire Mine	99	112	0.83	0.33	0.1	131.6	63.9	0.88	2.5	2.1	1.50	31	5.6	Pyrite, chlorite, gouge (unidentified).
48	Wentworth vein, Empire Mine	87	105	0.90	0.55	3.2	88.9	81.6	0.83	1.6	1.1	1.41	20	3.0	Calcite, chlorite, pyrite, gouge (unidentified).
49	Newmont vein, Empire Mine	99	114	1.25	0.45	0.05	56.1	79.0	0.87	2.8	0.7	1.48	34	1.9	Pyrite, chlorite, gouge (unidentified).

* Analysis subject to limitations—see text.

through the quartz (60, p. 353). Their formation thus *might* be contemporaneous with the deposition of the gold, which in many gold-quartz veins is also considered to be a later introduction (33).

Six samples from six different veins in the Grass Valley, Calif., gold-quartz district were run. These samples were obtained through the courtesy of Mr. H. R. Fitzpatrick, General Manager of the Empire Star Mines, to whom I wish to express my appreciation. The results on the series of samples are summarized in Table 3.

Although it is obvious that verification by study of additional samples from each vein taken across the width of the vein as well as from the same vein at other locations in the mine would be desirable, the differences between the fluids in the inclusions in these samples seem to be significant and may possibly be used to characterize samples, of unknown affiliations, as belonging to one or another of the veins. The Na/K ratios are all in the range 0.93 ± 0.10 although the differences may be greater than the experimental errors. The most significant variations are in the amounts and ratios of the rarer alkalies Li^+, Rb^+, and Cs^+. The amount of Cs^+ found in the Wentworth vein (No. 48, 3.2 mg) is ten times that found in the North Star vein (No. 44, 0.32 mg), and that amount in turn is considerably larger than that in any other sample run from this or other areas. Horstman (32) found the ratio K/Cs in igneous rocks to be 7,000. In the inclusion fluids represented by Table 3, the ratio K/Cs is as low as 33, indicating considerable enrichment in cesium in these fluids. As in Series 1, the Cl/SO_4 ratios may possibly reflect contamination from sulfides in the sample,[24a] and must be viewed with suspicion until further work is done, particularly as Wahler (64), and Zakharchenko (68), found very high Cl/SO_4 ratios in analyses of inclusions in quartz, beryl, and topaz. The anion/cation ratios that may be calculated from Table 3 indicate that another anion, presumably CO_2 as HCO_3^- or $CO_3^=$, must be present.[25]

[24a] Lindgren (43, p. 130–131) studied the composition of the fluid inclusions in a gold-quartz vein from the nearby Providence mine, Nevada City, California. He leached some of the powdered gold-quartz, containing pyrite, with cold water for two days, followed by three hours on the water bath; the soluble salts in the filtrate yielded the following, in grams per ton of quartz:

SiO_2	28	$(K,Na)_2O$	29
Al_2O_3, Fe_2O_3	2	SO_3	78
CaO	44	Cl	5
MgO	1		187

Lindgren states (43, p. 131), "The sulfuric acid could not have been derived from the pyrite, for there is scarcely any iron present. In all probability the soluble salts were contained in the fluid inclusions." As the original volume on filtration was 1,000 ml, it is evident that this amount of sulfuric acid could well have been in equilibrium with precipitated ferric hydroxide, and have come from the decomposition of pyrite. In view of the common occurrence of silver-bearing sulfide minerals in some of these veins, it might also be possible to reconcile Lindgren's report of low chloride content with the data presented here on the Grass Valley veins by assuming precipitation of part of the chloride by silver released from decomposing sulfides in his leach.

[25] Courtis (15, p. 639) reports that a sample of gold-quartz from another locality, the Tiger mine in Calaveras County, California, showed inclusions containing liquid CO_2. A number of other studies have been made showing the presence of CO_2, as a gas, as a liquid, as soluble carbonates, and as solid carbonates, in fluid inclusions (55). In many of the analytical determinations of CO_2 in the inclusions in rocks, however, there is no assurance given that small amounts of calcite were not present in the analyzed sample (See for example, Khitárov and Rengárten, 38).

OTHER TECHNIQUES

The ball milling-electrodialysis procedure described above has several shortcomings; perhaps the most serious is the inability to determine H_2O and CO_2 with it very effectively. Although it is possible to ball mill in an anhydrous, CO_2-free environment, and then analyze for H_2O and CO_2, it is awkward experimentally (36). It was thought that it might be possible to heat a sample of -10 $+48$ mesh quartz to decrepitate the inclusions, in a gas absorption train, and weigh the evolved H_2O, CO_2, and possibly H_2S.[26] The nonvolatile salts left behind from these decrepitated inclusions could then be removed for analysis by the same electrolytic cleaning method used to clean the original sample.

Theoretically this decrepitation technique could yield more information than a composite analysis of all the inclusions in a given sample using the ball milling procedure. The reason for this lies in the basic premise of the "decrepitation method" of determining the temperature of deposition of samples (53, 47, 48): if two different epochs of crystal growth or cementation have taken place at different pressures and/or temperatures, yielding two different sets of inclusions, the degree of filling of these two will probably be different, and hence they will decrepitate at different temperatures on reheating. There has been considerable discussion in the mineralogical literature about the relations between (1) the actual temperature of formation, (2) the temperature at which the liquid portion of a two-phase (liquid-vapor) inclusion has expanded to eliminate the vapor phase, and (3) the temperature at which the vapor pressure developed in the inclusion is adequate to rupture the quartz. The precision and accuracy of measurement of the temperatures of deposition of natural quartz crystals by this method are seriously dependent upon these relations, as well as on several other variables such as the size and spatial distribution of the inclusions. Although these many variables place rather drastic limitations on the decrepitation method for geothermometry, they have less effect on the usefulness of the decrepitation method in determining the composition of the inclusion liquids from the two or more epochs of crystal growth or cementation involved. If the degree of filling of the two sets of inclusions is sufficiently different, the bulk of the one set could be opened by decrepitation and the evolved gases analyzed; the sample could then be electrolytically cleaned to obtain the nonvolatile elements from these inclusions, and the process repeated with a higher temperature decrepitation to open the other set of inclusions. The discrimination between the sets of inclusions by this method is limited, of course, by all the variables that may affect the temperature of decrepitation.

To try this decrepitation method a simple gas absorption train was set up as shown schematically in Figure 6. Pure nitrogen at atmospheric pressure was used as the flushing agent (50, p. 448). To avoid possibility of error from differences in the vapor pressures of H_2O and CO_2 remaining in the nitrogen on entering and leaving the train, the gas was equilibrated with the

[26] Crushing in a stream of dry air was used by Pfaff (49).

absorbents used before it entered the sample flask. This flask was a long-necked, round-bottomed, one-liter flask of clear fused silica, and was heated with a flask heater made with fused silica fabric insulation to permit operation at higher temperatures (above 500° C). A layer of glass beads was placed in the bottom of the sample flask to distribute the nitrogen flow, and a high-temperature mercury thermometer was centered in the quartz sample. The heating rates used were small enough (<1°/min) to avoid sizable differences between the central thermometer and a thermocouple placed against the outside surface of the flask. The exit gases from the flask could be switched into either of two absorption trains, each made of weighed Schwartz U tubes, so that operation could be continuous and differences in the amount or composi-

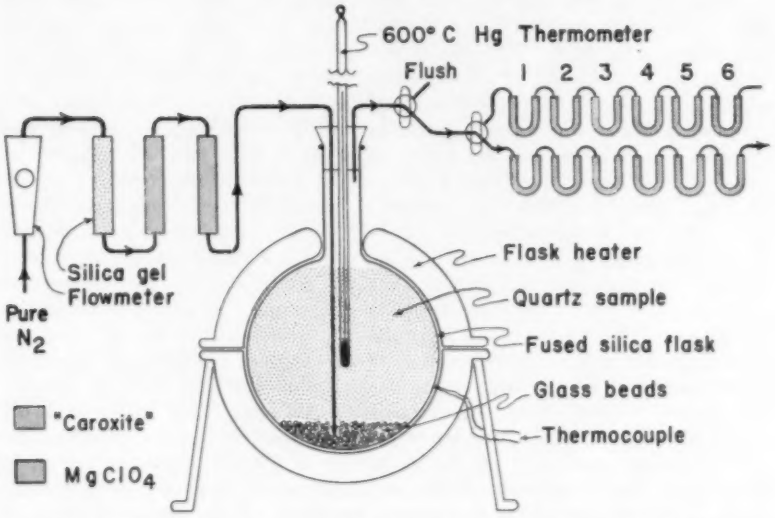

FIG. 6. Diagram of apparatus for decrepitation in an absorption train. The purification train for the nitrogen is not shown.

tion of the gases evolved with time or temperature could be determined. All absorption tubes were equipped with individual stopcocks to prevent loss or gain from the air before or after weighing; these were opened for ten seconds before weighing to release any nitrogen pressure and to decrease the magnitude of the barometric pressure corrections to be made in the weighings. The first U tube, containing $MgClO_4$, takes out the water from the inclusions; the third U tube with "Caroxite" (NaOH on a granular extender) removes the CO_2; and the fifth U tube takes out the H_2O formed in the third tube (beyond that removed by the NaOH itself). Each absorption U tube is backed up with a duplicate for checking purposes. The individual tubes, fitted with wire hangers for hanging from the balance stirrup, weigh only 65–80 grams, permitting weighing to a precision of ±0.0002 g. This is better than is

needed, considering the precision of the determinations as estimated by adding known amounts of H_2O or $KHCO_3$ to a blank sample in the flask.

The electrolytically clean sample, weighing approximately 1 kilogram, is heated to 110° C and a flow of 100 cm³ nitrogen per minute passed over it to remove adsorbed water on the surface. According to Kunkel (41), well-cleaned quartz surfaces have only one or two layers of water molecules which should amount to only a few milligrams of water per kilogram of −10 +48 mesh material. A vacuum drying would be more desirable, however, as the true surface area of coarse material of this type may be much greater than the apparent external surface of the grains, owing to lineage cracks and other defects. After drying at 110° C, the temperature is raised slowly, with a constant flow of nitrogen, to the desired temperature. When no further H_2O or CO_2 is evolved, the temperature is raised again.

Time permitted only one run to be made with this procedure,[27] on 815 grams of quartz sample No. 48, from the Wentworth vein, Empire Mine, Grass Valley, California. Only one heating cycle was used, heating to 488° C

TABLE 4

COMPARISON OF RESULTS OF ANALYSIS OF MATERIALS IN FLUID INCLUSIONS OF SAMPLE NO. 48, BY TWO DIFFERENT METHODS

	Ball milling-electrodialysis (from Table 2)	Decrepitation-absorption-electrolysis*
Na^+	87	4.3
K^+	105	2.7
Cl^-	88.9	24.3
$SO_4^=$	81.6	37.7
CO_2	—	0.06
H_2O	—	1.93

* Recalculated to a 1,000 gram sample for purposes of comparison with the other results.

(on the central thermometer) during a 23-hour period. A total of 1.570 g. of H_2O and 0.050 g. of CO_2 was obtained.

After the decrepitation, the quartz sample was put into an electrolytic cleaning tube and the inside of the flask flushed out with deionized water. This water was also placed in the tube, and a current passed through it, as in the electrolytic cleaning, except that the solutions from around the anode and cathode were saved and analyzed, as in the electrodialysis cell. The results were surprisingly low, however, as shown in Table 4.

There are several possible explanations for the discrepancies in these results, but none of these explanations have been verified. First, it is possible that the inclusions lost their volatile H_2O and CO_2 during decrepitation without much breaking open of the vacuoles. This emptying of vacuoles without the formation of visible cracks has been noted before (59, p. 51; 53, p. 648; 54, p. 547), and would make the removal of any nonvolatile chlorides and sulfates remaining in the cavities very difficult.[28] Second, any reaction

[27] This was run by Lloyd L. Ames, Jr.

[28] Even volatile materials are difficult to get out of these cracked inclusions. A sample that had been decrepitated was wet with water and dried overnight at 110° C with the nitrogen flowing. On raising the temperature further, to its previous decrepitation temperature, Ames

of the nonvolatile salts with the quartz surface could result in the formation of silicates and HCl or H_2SO_4. The HCl would go through to the absorption train, but the H_2SO_4 would condense on the neck of the flask and in the tubing. Although the Cl^- and at least a part of the $SO_4^=$ would be lost, the silicates should presumably be broken up by the electrolytic cleaning process if they were accessible. However, at the temperature of this run, the rates of diffusion of alkali ions in quartz become appreciable (62), and at least some portion of the alkalies could diffuse into the quartz surfaces far enough to preclude recovery on electrolysis.

If these results cannot be improved, they make the decrepitation procedure less useful than anticipated in the analysis of fluid inclusions, but still the determination of H_2O and CO_2 by this procedure could be combined with cation and anion determinations by the ball milling procedure. *If* it can be assumed that all inclusions were opened in both runs, and that only one set of inclusions was present,[29] the inclusions in sample 48 would have in gross composition a water solution containing 18 percent, by weight, of sodium and potassium chlorides, sulfates, and carbonates.

It is apparent from the above that decrepitation itself, although useful for giving the composition of the volatile materials in fluid inclusions, has serious limitations. If the ball milling-electrodialysis technique could be revised to determine total CO_2, some differentiation between CO_2 from liquid carbon dioxide and that from the carbonate radical might be possible by comparing the CO_2 analyses by the two methods. Another possible method of differentiation between these two materials involves crushing in oil between glass plates under the microscope (18, 19, 20); this technique might also give some hint on the discrimination between free CO_2 and the bicarbonate ion.[30]

There has been a considerably increased application of isotopic ratios to the solution of geological problems in the last few years. Several reasons indicate that the ratios between the isotopes of each of the light elements expected in inclusions (H, C, O, and S) should vary. The decrepitation method should yield samples suitable for such isotopic studies.

CONCLUSIONS

A method has been developed for the extraction and partial chemical analysis of the ionic constituents in the fluid in microscopic fluid-filled inclusions in quartz and other minerals. The essential features are ball milling and electrodialysis, done with considerable care to avoid loss or contamination. Many possible refinements and cross checks that might be made on the method are evident. The method is most useful for the determination of the ratios of the alkali metals in the inclusions, and, with greater limitations, for the

found that 147 milligrams of water came off. This presumably came from inclusions that had been refilled by capillarity, as the amount of surface area available after decrepitation, even including the cracks, is only adequate to yield a milligram or two of water.

[29] Ferguson and Gannett (23) found two sets in the nearby Allegheny district lode deposits.

[30] Infrared (and ultraviolet) absorption techniques might also be applicable here in thin plates including the fluid inclusions.

determination of the ratios of Cl^- to $SO_4^=$. A series of analyses show that even this limited information may possibly be of use in the solution of geological problems. Even if a perfect technique for extraction and analysis were developed, the interpretation of results would be subject to serious limitations, in particular the possibility of multiple generations of inclusions in a sample, and the possibility of loss or gain of materials by leakage or diffusion. This very ambiguity of origin of the inclusions may eventually be investigated with the method developed, however, and may become helpful in delineating the history of the fluids from a sample or region. In particular, the combination of this method with other methods such as decrepitation in an absorption train, where H_2O and CO_2 may be determined, yields data on concentrations, but only with an increase in possible ambiguity.

The results to date indicate that an as yet untried method—involving coarse dry ball milling in an absorption train, followed by electrodialysis of the resultant powder—may be the most suitable for future studies. For many reasons, it may also be best to reduce the whole operation to a microchemical analysis scale, where the selection, control, and observation of the sample used could be more effective.

U. S. Geological Survey,
Washington, D. C.,
Nov. 12, 1957

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STRUCTURAL SECTIONS AND THE THIRD DIMENSION

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ABSTRACT

Conventional structural sections inadequately portray geometrical relations. A plane is represented by its trace line, an ambiguous procedure which on structural maps is clarified by adding the dip symbol and figure. The acute angle between a structural plane and a vertical plane of section is now termed the *angle of departure*. It is measured in a plane normal to the trace line. This angle relates the structure to the vertical section just as the dip relates it to the (horizontal) map. The departure is expressed as a function of the strike intersection and apparent dip. Reference of the two latter angles to an alignment diagram therefore gives the angle of departure. Commonly a simple graphic-trigonometric solution suffices.

Conventional sections omit lineations altogether: fold axes, mineral alignments, preferred orientations, etc. Their introduction to structural sections is also feasible and should be clarifying. The normal projection of the lineation must first be plotted on the section. The term *apparent plunge* is proposed for the inclination which such a normal projection will assume on the vertical section. The minimum angle between the lineation and the plane of section, now termed the *angle of penetration*, compares to the angle of plunge of the geologic map. The apparent plunge and angle of penetration are derived, expressed as functions of known angles, and presented as alignment diagrams.

This system permits structural sections to express available data in three dimensions as effectively as structural maps. The similarity of such augmented sections to structural maps facilitates their study.

INTRODUCTION

THE first compilation of the geology of a district is commonly made on a structural map. As structural studies proceed, data are often presented by maps supported by structural sections, or possibly by models or isometric drawings. Where it is desirable to use but one drawing, however, the choice is usually between a structural map and a vertical structural section. These two alternatives therefore merit comparison.

In areas lacking sub-surface data, the structural map has the advantage of displaying simultaneously all facts and observations and embracing the entire region of study. This advantage is partially dissipated if drilling or underground mining results in the accumulation of a comparable amount of data.

It is noted that the most effective expression of structure is obtained by construction of a drawing perpendicular to the significant structural trends. In this consideration the section is usually superior to the map, for it can be placed and oriented where most effective, though it is rarely other than vertical. The map, in comparison, is limited to a single orientation, i.e. horizontal, although a choice of elevations is sometimes had, as in mining geology.

The structural map has to date enjoyed one more large advantage. Its strike and dip symbol for planes and its comparable designation of lineations have to some extent given it three-dimensional expression. The possibility of sharing these procedures with the structural section has led to the present investigation. Given equality in this regard, the vertical structural section should become a much more effective medium for illustrating geologic structure.

The foregoing remarks have served to recall that the familiar strike and dip symbol, which we so take for granted on the structural map, actually performs a most singular function: to some extent it conveys a three dimensional view of structural relations. Where geologic study includes linear features, these are comparably expressed by inclusion on the map of their bearings and plunges.

Despite the effectiveness of these procedures on maps, however, structural sections to date have apparently not included their corollaries: i.e. procedures which would relate structural planes and lines to the vertical section in the manner that they now relate to the horizontal on the map.

The use of such devices on sections would clarify the presentation of planes, which, as will be shown below, are otherwise indicated ambiguously. Lineations could be expressed in the fullness of their three dimensional relations; to date they apparently have been omitted from sections. Structural sections could be studied with much less reference to related maps or sections. In some studies a more complete realization of the three-dimensional relations of structural planes and lineations should materially clarify structural problems. These several advantages suggest the desirability of including on the section, if possible, symbols and angular readings comparable to strike and dip data, and, for lineations, to bearing and plunge data.

For the sake of consistency, reference will always be to that part of the structure which is beyond the structural section, as is true where a cliff is

viewed. This convention is consistent with standard mapping practice, where reference is always to that part of the structure which is beyond the plane of mapping, i.e. below ground.

POSSIBILITY OF PRIOR WORK

Search of the limited literature at hand has not disclosed previous definition or derivation of the three angles basic to the present discussion. It seems very likely that the two lineation angles have at some time been resolved to facilitate plotting of drill holes. There has clearly been no general acceptance, however, of the methods now advocated. Thus the present study was undertaken to show the advisability of expressing these three angles and to offer some assistance in their routine determination. If any of these angles have been previously defined or derived in the literature for structural purposes, apologies are in order.

STRUCTURAL PLANES

Expression of Structural Planes.—The first expression of a structural plane on a geologic map or structural section is by its line of intersection. This line of itself is quite ambiguous, for it might equally well represent any of the family of planes generated by a plane rotating about this line as an axis. On the structural map this is clarified by the addition of the dip symbol and figure. By this device a single map effectively expresses the three dimensional relations of relatively complex structure. In contrast, the structural section must be complemented by a map or an additional section, the alternative being ambiguity. Unfortunately the structural section has not always been supplemented in either manner, due perhaps in some cases to space limitations during publication. Ambiguity has therefore been quite common.

It may prove instructive to speculate here as to why the dip symbol developed on the structural map, whereas its corollary did not develop on the structural section. Doubtless one significant point was that deviations from the plane of the geologic map, i.e. the horizontal, could be directly measured with the readily available clinometer. No comparably simple procedure was available for measurement of the angle between a structural plane and a vertical cliff or mine wall.[1]

Actually, however, most vertical sections are not compiled from direct observations. Rather, they are developed from other sources of data, such as surface maps, mine level maps, and drill hole intersections. The present discussion will develop the geometrical procedure for the conversion of these generally available data to an angular measurement which compares to the structural map's dip figure. The term *angle of departure* is proposed for this measurement, which is the acute angle between a structural plane and a vertical section. It is measured in a plane perpendicular to the line of trace. The angle of departure therefore relates a structure to the vertical plane in a manner geometrically identical to that of the angle of dip where the latter relates the structure to the horizontal. The angle of departure, in further analogy to the

[1] This difficulty is referred to more fully below. See "Possibility of direct measurements."

dip, is plotted on the section with a barbed arrow (or the equivalent unbarbed lead, as in Fig. 3) affixed to the line of trace to indicate the direction of departure. This symbol, with its adjoining angular notation, should be as expressive on the section of the third dimension as the familiar dip symbol is on the structural map.

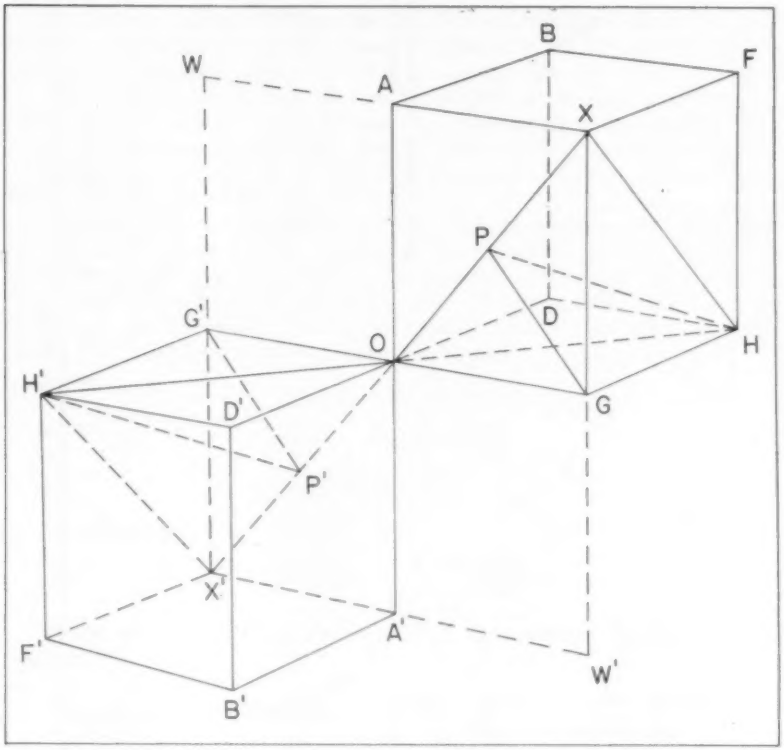

FIG. 1. Relations of a structural plane, XHOH'X' to a vertical plane of section WXW'X'.

In the upper, right-hand block segment XOH represents structures that dip away from the section. The pertinent angles are: apparent dip, AXO; acute strike intersection, GOH; and angle of departure, GPH.

The lower, left-hand block represents structures that dip toward the section. The two blocks are congruent so that the above identifications maintain in this block also.

Trigonometric Solution for Angle of Departure.—Figure 1 is a perspective drawing of two adjacent blocks, both of which adjoin a common vertical plane WXW'X'. These blocks illustrate the two basic types of inclined structures in their relations to a vertical structural section. To the right and behind the

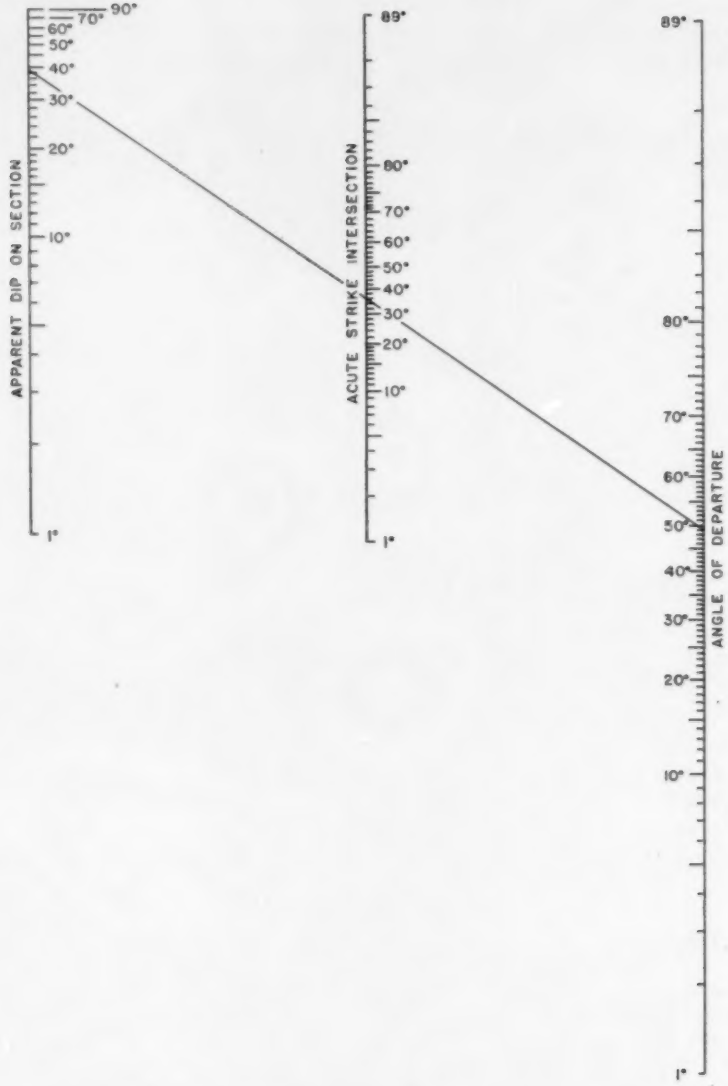

FIG. 2. Alignment drawing for angle of departure. In the ruled example an apparent dip of 39 degrees and an acute strike intersection of 36 degrees indicate 49 degrees for the angle of departure.

Structures which on the map dip toward the vertical section have departures

vertical section, plane XOH represents structures which dip away from the vertical section. To the left and in front, plane X′OH′ represents structures that dip toward the vertical section. In each of the following treatments the angle of departure will be determined for the first of these types, i.e. for structures dipping away from the section. A modified solution will then be indicated for structures that dip toward the section.

In the upper portion of Figure 1, AXOG represents the vertical structural section. The upper and lower planes of this block, i.e. BFAX and DHOG, are horizontal. A structural plane dipping away from the section is represented by XOH. Therefore the line of strike is HO; the acute strike intersection is angle GOH; the line of trace is XO; and the apparent dip is angle AXO. The angle of departure, or the acute angle between the structural plane and the vertical section is angle GPH, which is illustrated by construction of plane GPH perpendicular to XO.

As plane GPH is perpendicular to XO, it is necessarily perpendicular to the plane of section AXOG. However, two planes (GPH and DHOG) which are perpendicular to a third plane (AXOG) can only intersect in a line that is also perpendicular to the third plane. By this maxim HG is perpendicular to AXOG and in further consequence to lines GP and GO. Triangles HGP and HGO are therefore right triangles. Continuing:

$$HG = GO \tan GOH$$

$$GP = GO \sin GOP$$

$$\text{Tan } GPH = \frac{HG}{GP}$$

Substituting:

$$\text{Tan } GPH = \frac{GO \tan GOH}{GO \sin GOP}$$

However angle GOP equals angle AXO, the apparent dip angle. Consequently:

$$\text{Tangent of angle of departure} = \frac{\text{Tangent of acute strike intersection}}{\text{Sine of apparent dip}}$$

The acute strike intersection and the apparent dip are known values.

The two blocks drawn in Figure 1 are congruent throughout. Thus all the geometrical relations noted above for the upper block maintain as well for the lower block, where plane X′OH′ represents structures that dip toward the vertical section.

The above solution for the angle of departure is presented as an alignment

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with an upward component; structures that dip away have departures with a downward component.

The drawing is a logarithmic plotting of the equation:

$$\text{Tangent departure} = \frac{\text{Tangent acute strike intersection}}{\text{Sine apparent dip}}$$

drawing in Figure 2, the use of which obviates reference to tables of functions. It is necessary to note whether in plan and on the far side of the section from the viewer a structure dips away from or toward the vertical section, for structures which in plan dip away from the section require a departure arrow with a downward component (Example A, Fig. 3), whereas structures which dip toward the section require an arrow with an upward component (Example D, Fig. 3).

Graphic-Trigonometric Solution for Angle of Departure.—It has been demonstrated above that in the upper portion of Figure 1 angle GPH is the angle of departure and that triangle HGP is a right triangle. These conditions relative to point H may also be demonstrated for any other point within

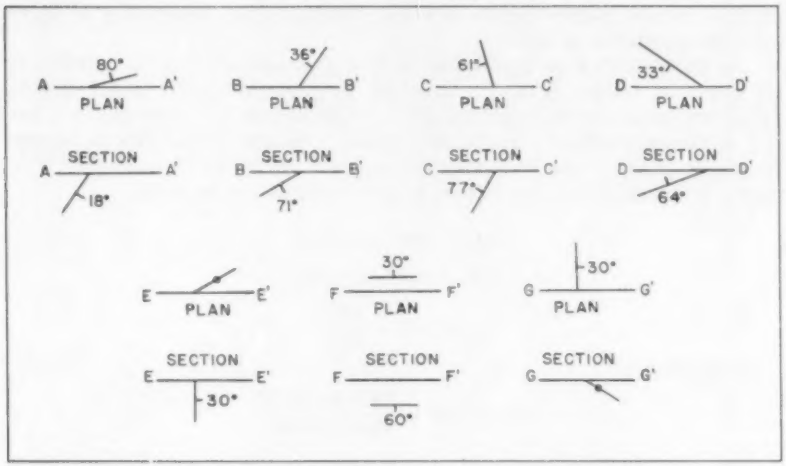

FIG. 3. Examples illustrating the angle of departure. Note throughout that where in plan a structure dips away from the section (Example A) the departure, on the section, is downward. Conversely, Example D illustrates a structure dipping toward the section resulting in an upward departure. In the last three examples sight solutions are possible. In Example G note the 90 degree departure is indicated by the same symbol used for the 90 degree dip of Example E.

the structural plane XOH. The following solution is therefore valid, based upon the expression tangent GPH = GH/GP.

On a map select any known point H within the plane of the structure. This point may be above or below the map plane, but must be of known elevation. From H draw line GH perpendicular to the plane of section, and measure the distance GH. Refer now to the sectional drawing, on which it is presumed the trace of the structure appears. On this section locate point G, which, to reaffirm, is equal in elevation to point H. From G draw line GP perpendicular to the line of trace XO, extending the line of trace if necessary. Measure the distance GP. The ratio GH/GP is the tangent of the angle of

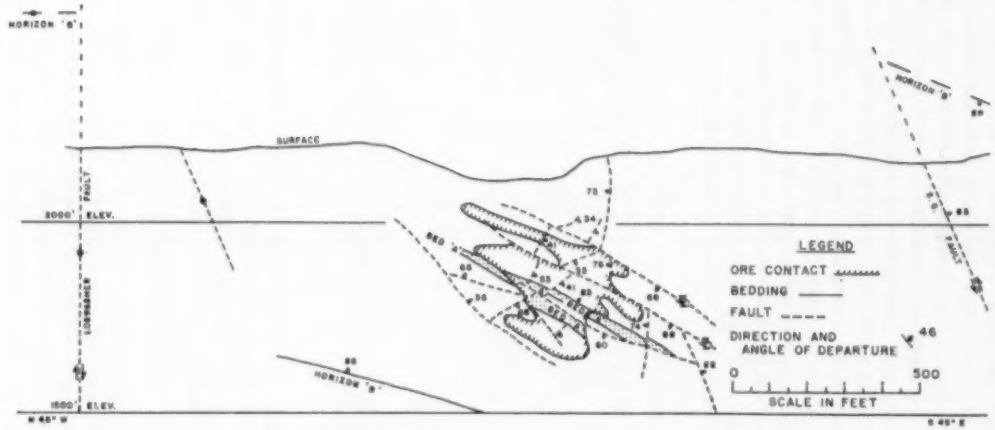

FIG. 4. Mine section at Austinville, Va., illustrating angle of departure. Each barbed arrow and adjoining numeral indicates the angle between a structural plane and the vertical plane of section. This usage is analogous to the use of the strike and dip symbol on a map.

The section, viewed facing northeast, is through the Austinville, Va., mine of The New Jersey Zinc Company. Ore, which trends northeasterly, consists of zinc, lead, and iron sulphides replacing a dolomite host rock. The basic structure is a graben, which results from movement on the Logwasher and Stamping Ground Faults. The graben is recognized from the several positions of Horizon B. Geology by staff geologists.

departure, GPH, which angle may be obtained from a table of functions, slide rule, or by graphic solution of triangle GPH.

It is noted here, again, that insofar as Figure 1 is congruent about point O the preceding solution for structures that dip away from the vertical section maintains also for structures that dip toward the section. The graphic-trigonometric solution for the angle of departure is brief, simple, easily remembered, relatively accurate, and independent of any special graph. These advantages recommend it highly where the available data permit its use.

Discussion.—Varied examples illustrating the angle of departure are shown in Figure 3. A structural section through the Austinville, Virginia, mine of The New Jersey Zinc Company is presented in Figure 4. In this example the angles of departure are added to the structures of an established mine section. Some workers may prefer to solve for the angle of departure by use of the stereographic method (2), which is quite adequate.

STRUCTURAL LINEATIONS

Expression of Structural Lineations.—The U. S. Geological Survey's Map Symbol Committee (5, 1948) has adopted the term "plunge" for the angle of any lineation measured in the vertical plane. This singleness of terminology, after years of confusion in the literature with "pitch," is most commendable and clarifying. It is particularly helpful in the present discussion, which must consider the geometry of all lineations concurrently, regardless of their geologic differences.

In the preceding pages it was concluded that structural planes have to date been inadequately represented on structural sections. Lineations, on the other hand, have apparently been omitted completely. This omission is inconsistent with their established utility in many varied studies having structural considerations. Thus Cloos (3, p. 45), in his authoritative review, concludes:

"Lineation . . . has become one of the tools by which directions of tectonic movements or pressure have been established." And elsewhere (3, p. 1), "Their orientations should appear on all geologic maps, together with other structural symbols."

McKinstry (7, p. 29), in specific reference to bedding, counsels:

"In highly contorted bedding, however, extremely accurate readings are not significant, since greatly varying dips might be obtained within a foot or two. In such cases the important thing to record is the form of the fold, rather than precise readings of dip, for the attitude of the axial plane and the plunge of the axial line are likely to be more significant than the local dip of the bedding."

It would seem that many structural problems would be clarified if studied in section with lineations properly included. It is therefore recommended that structural sections include lineations, and that their full three-dimensional relations be indicated.

It may be instructive here to compare the geometrical representation on structural sections of planar and linear elements, as practiced to date and as

now proposed. The structural plane intersects the vertical section as a line of trace, which has conventionally been plotted. Its inclination is the familiar apparent dip. The present discussion has added the concept of the angle of departure to designate the structure's intersection with the section. In comparison, the structural lineation intersects the vertical section as a mere point, the plotting of which per se would be quite meaningless in conveying the line's orientation. Conventional structural sections therefore omit the lineation altogether. It can, none-the-less, be projected to the section. It is therefore proposed that the lineation be represented on the structural section by its normal projection, in analogy to its usual projection to the horizontal plane in mapping. The term *apparent plunge* is proposed for the inclination that such a normal projection of a lineation will assume in the plane of section.

It has been noted above that the plotting of a plane on section by its trace line alone results in ambiguity. The plotting of a lineation by its apparent plunge alone would result in comparable ambiguity: that is to say, the third dimension would not be indicated. For the structural lineation, therefore, a further concept is now introduced, that of the *angle of penetration,* or the minimum angle between the linear element and the vertical plane to which it is projected. Restated, this is the angle between the lineation and its apparent plunge line. The angle of penetration relates the lineation to the vertical section just as the angle of plunge relates it to the (horizontal) map.

Trigonometric derivations of the above two angles follow, first for the angle of apparent plunge. It seems likely that these rather obvious solutions have been demonstrated previously, for example, to permit adequate plotting on a structural section of inclined drill holes whose bearings do not parallel that of the section.

Trigonometric Solution for Angle of Apparent Plunge.—Figure 5 is a perspective block drawing of the relations of a lineation to a vertical section. The section, XDD′X′, is intersected at O by AOA′, representing the general case of an inclined linear element. To the right in the drawing, AO represents a lineation plunging toward the section. To the left, extension A′O represents a lineation plunging away from the section. These two segments, AO and A′O, have congruent relations to the vertical section. Therefore the following demonstration of the relations of AO to section XDD′X′, i.e. a lineation that plunges toward the section, is applicable to A′O, i.e. a lineation which plunges away from the section.

In Figure 5, HA is the horizontal projection of AO, consequently angle HAO is the plunge of AO. Through A, AD is constructed perpendicular to the section, and the points H and D connected. Angle AHD is then the acute bearing intersection of AO with respect to the vertical section. DO is also drawn, the normal projection on section of AO. Angle HDO is therefore the apparent plunge of AO, in accordance with the definition stated previously.

Continuing:

$$1)\ \text{Tan HDO} = \frac{\text{HO}}{\text{HD}}$$

$$2)\ \text{HO} = \text{HA Tan HAO}$$

$$3)\ \text{HD} = \text{HA Cos AHD}$$

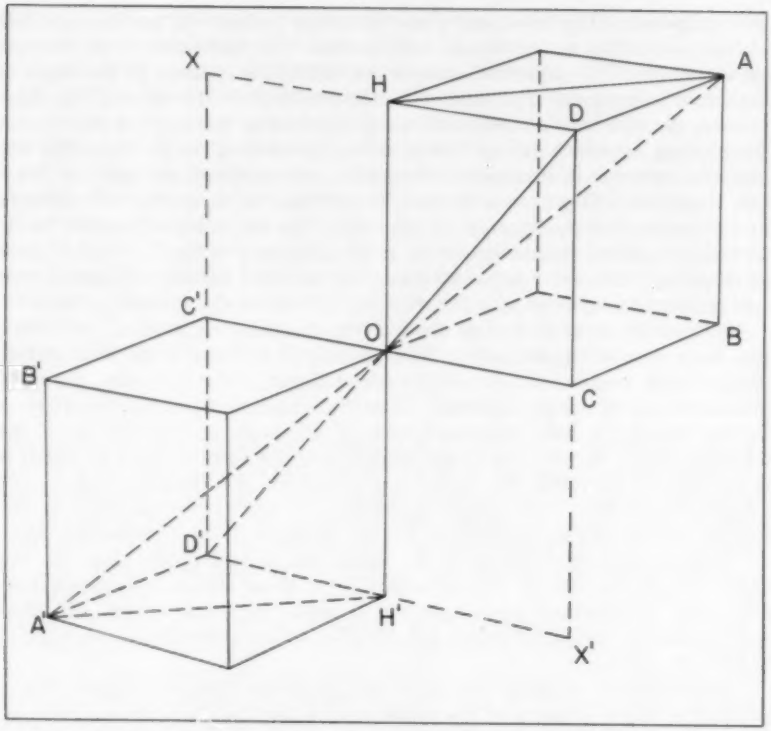

FIG. 5. Relations of a structural lineation, AOA′, to a vertical plane of section, XDD′X′.

In the upper, right-hand block segment AO represents lineations that plunge toward the section. The pertinent angles are: plunge, HAO; acute intersection of bearing, AHD; apparent plunge, HDO; angle of penetration, AOD.

The lower, left-hand block shows the segment A′O, which represents lineations which plunge away from the section. Insofar as the two blocks are congruent the identifications noted above maintain in the lower block as well.

Substituting (2) and (3) in (1):

$$\text{Tan HDO} = \frac{\text{HA Tan HAO}}{\text{HA Cos AHD}}$$

Therefore:

$$\text{Tangent of apparent plunge} = \frac{\text{Tangent of plunge}}{\text{Cosine of acute bearing intersection}}$$

This expression for the angle of apparent plunge is presented as an alignment drawing in Figure 6, the use of which obviates reference to tables of functions.

Trigonometric Solution for Angle of Penetration.—In conformity with the definition proposed above, angle AOD in Figure 5 is the angle of penetration. This is derived as follows:

$$1)\ AO = \frac{HA}{\text{Cos } HAO}$$

$$2)\ AO = \frac{AD}{\text{Sin } AOD}$$

FIG. 6. Alignment drawing for apparent plunge. In the ruled example an acute bearing intersection of 65 degrees and a plunge of 20 degrees indicate that the apparent plunge on section is 41 degrees. This drawing, based on natural functions, is a plotting of the equation:

$$\text{Tangent apparent plunge} = \frac{\text{Tangent plunge}}{\text{Cosine acute bearing intersection}}$$

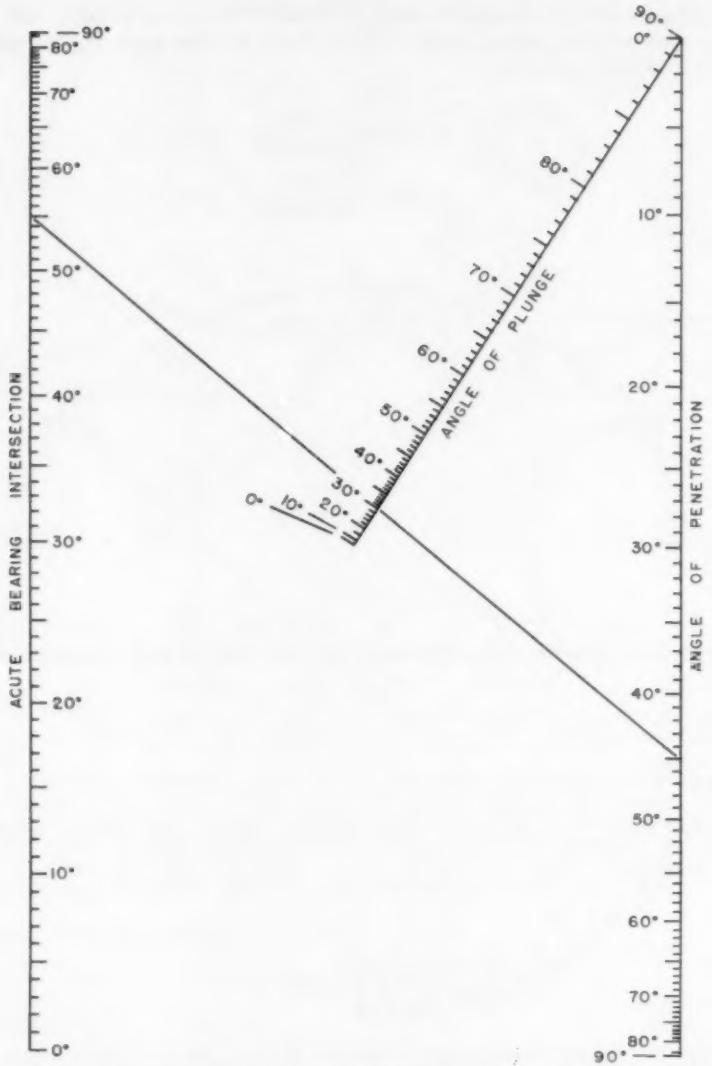

FIG. 7. Alignment drawing for angle of penetration. In the ruled example the acute angle between the bearing and the section is 55 degrees. The plunge is 30 degrees. The lineation therefore has an angle of penetration of 45 degrees.

Lineations which, on the map, plunge away from the section have a downward component in sectional treatment. Those that dip toward the section have an upward component on the section. The drawing, based on natural functions, is a plotting of the equation:

Sine of penetration = Sine of acute bearing intersection × Cosine of plunge

Equating (1) and (2) and continuing:

$$\frac{HA}{\text{Cos HAO}} = \frac{AD}{\text{Sin AOD}}$$

$$\text{Sin AOD} = \frac{AD \text{ Cos HAO}}{HA}$$

$$\text{Sin AOD} = \text{Sin AHD Cos HAO}$$

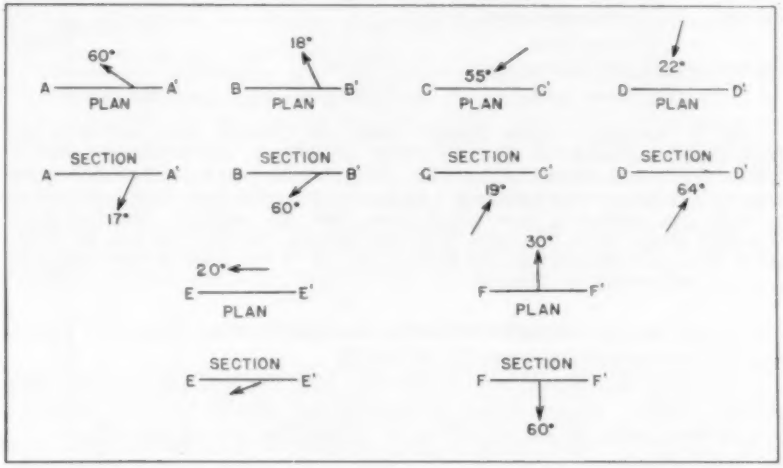

FIG. 8. Examples of lineations recorded on section by plotting their apparent plunges and indicating numerically their angles of penetration. An inconsistency of treatment may be noted for lineations that in plan plunge toward the section, as example D, for the arrow barb's position in section is reversed from its position in plan. This is unimportant. It results from the conventional omission of polarity in recording lineations. Thus, in conventional mapping all lineations are considered to plunge downward from the mapping plane; and extension of this convention to the present sections results in considering all lineations to leave the section while going away from the observer. A similar inconsistency relates to the arrows of the symbols expressing planes, but seems less confusing there.

Therefore:

Sine of angle of penetration = Sine of acute bearing intersection
× Cosine of plunge.

These relations are expressed as an alignment drawing in Figure 7, the use of which obviates reference to tables of functions.

Determinations of the angle of apparent plunge and the angle of penetration are quite simple and amenable to other methods of resolution. In Figure 8 several examples of lineations are plotted in section in accordance with the present discussion. As a field example, Figure 9 is also included. This is

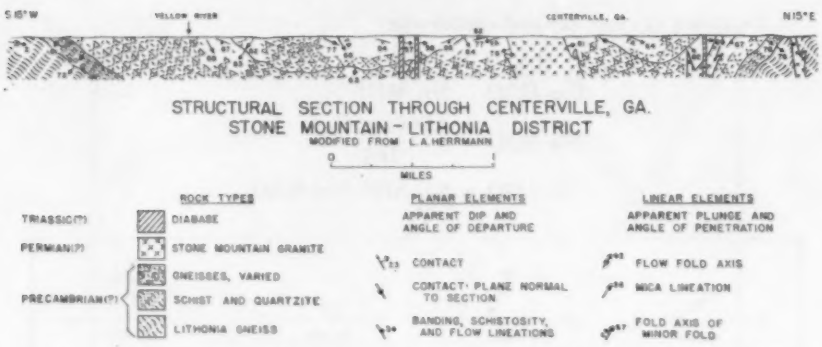

FIG. 9. Structural section through Centerville, Georgia, Stone Mountain district, illustrating angles of apparent plunge, penetration, and departure. Section trends N15E and is viewed looking west. Section based upon published data, using alignment drawings of present text. As emphasis is upon illustrating a variety of symbols, the section is generalized more than the original. Modified from "Geology of the Stone Mountain—Lithonia District, Georgia," by Leo A. Herrmann, Georgia Geological Survey Bulletin No. 61. Permission of Herrmann and Garland Peyton, Survey Director.

a structural section through Centerville, Georgia, in which linear and planar elements are indicated as presently advocated.

Mining geologists will note incidentally that the methods presently discussed to indicate the orientation of lineations are suitable for the representation on the vertical section of inclined drill holes that are not parallel in bearing to the section.

DISCUSSION

Suggested Symbols.—This study has indicated the manner of including on the structural section all types of structural planes and lineations: i.e., respectively, beds, faults, joints, cleavages, etc.; and fold axes, primary and secondary flowage, slippage, etc. Inclusion of these varied planes and lineations on the structural section requires the selection of suitable symbols. An obvious alternative, recommended herewith, is to include on the section all the standard structural symbols currently used on the geologic map, as the symbols for cleavage, fold axes, etc. This simple expediency will almost completely obviate the introduction of new symbols and will facilitate easy reading of the new type of structural section from the start.

Possibility of Direct Measurements.—It seems appropriate to consider the feasibility of measuring directly the angles of departure and penetration, as, for example, in mapping mine raises. Before doing so it will be instructive to consider the analogous problems in regular mapping, i.e., reading the angles of dip and plunge. These latter two angles are vertical angles. Consequently, they may be read by reference to the horizontal, which is conveniently defined by the level of the clinometer.

In unfortunate contrast, the angles of departure and penetration are

vertical angles only in special cases. Thus, they cannot usually be read by simple reference to the (level-defined) horizontal. Possibly a protractor device might be designed for direct measurement of the angles of departure and penetration. It seems now, however, that such an instrument would lack the quick accuracy of the clinometer.

It should be noted, none-the-less, that direct measurements, if ever made feasible, should have greater accuracy than alignment drawings normally afford. As recalled earlier in this study, however, structural sections usually result from office compilation rather than from direct observation. Thus, the lack of methods for directly measuring these angles will not usually be noticed.

Alternative Expression of Planes.—Examination was also made of an alternative method of expressing the third dimension of structural planes in vertical section. In this method the acute strike intersection of the structure is read from the map and indicated numerically on the section. Apparently this procedure is not always completely effective in conveying a sense of the third dimension. Moreover, the consistent extension of this practice to express lineations is cumbersome if not confusing. Thus the procedure seems generally unsuitable for either planes or lineations, though in special, restricted studies it might have some advantages in expressing planes.

CONCLUSIONS AND RECOMMENDATIONS

It is feasible to add to the structural section symbols that compare to those used on the structural map to indicate the strikes and dips of planes and the bearings and plunges of lineations. The angle of departure is defined as the acute angle between a structural plane and a vertical plane of section. It is measured in a plane normal to the trace line. It is demonstrated that:

$$\text{Tangent of departure} = \frac{\text{Tangent of acute strike intersection}}{\text{Sine of apparent dip}}$$

These relations are presented as an alignment drawing. A second solution using graphic-trigonometric methods is also given.

For lineations it is shown that:

$$\text{Tangent of apparent plunge} = \frac{\text{Tangent of plunge}}{\text{Cosine of acute bearing intersection}}$$

and also that:

$$\text{Sine of angle of penetration} = \text{Sine of acute bearing intersection} \times \text{Cosine of plunge}$$

These two formulas for linear elements are also expressed as alignment drawings.

It is recommended that future structural sections express the angles of departure for planes, and that lineations be included by plotting their apparent plunges and indicating their angles of penetration. By these procedures the structural section will be made equal to the structural map in its ability to express both planar and linear elements in three dimensions.

It is further recommended that the symbols conventionally used on the map for various planar and linear elements be adapted to the structural section. This will promote immediate comprehension of the new type of section by the profession and avoid the needless burden of learning new symbols.

In conclusion it is noted that the chore of supplementing the structural section as now advocated, although not great, lies wholly with the geologist-draftsman. Assimilation of the new data by the reader requires no special preparation.

ACKNOWLEDGMENTS

The writer is grateful to Owen Kingman of the Tennessee Copper Corporation for early encouragement and suggestions. The New Jersey Zinc Company kindly permitted inclusion of the section through its Austinville, Virginia, mine and provided varied assistance throughout. M. L. Fuller of The New Jersey Zinc Company verified the mathematical basis of the discussion. W. Horatio Brown of this company offered helpful suggestions. Thanks are also due to Leo A. Herrmann and the Georgia Geological Survey for permission to modify a section selected from Herrmann's Stone Mountain-Lithonia District report. Particular appreciation is expressed to Prof. G. M. Schwartz and to Richard B. Taylor for their thorough review and criticism of the manuscript. Prof. Marland P. Billings kindly reviewed the study in its later form.

THE NEW JERSEY ZINC COMPANY,
AUSTINVILLE, VIRGINIA,
Oct. 1, 1957

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DEUTERIC ALTERATION OF SOME APLITE–PEGMATITES OF THE BOULDER BATHOLITH, MONTANA, AND ITS POSSIBLE SIGNIFICANCE TO ORE DEPOSITION[1]

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ABSTRACT

The Boulder batholith contains many texturally complex leucogranitic aplite-pegmatite intrusives. Both the aplite-pegmatites and the enclosing quartz monzonites were hydrothermally altered along steep zones of closely spaced fractures that are in part the hosts for vein deposits. Mineralogically and chemically similar alterations of different origin are common in some aplite-pegmatite intrusives near Boulder, Mont. These internal alterations are small, irregular, and vaguely outlined and are commonly related spatially to pegmatitic textures. The altered rocks were formed during crystallization of the aplite-pegmatites and are thus deuteric in nature. These deuteric alterations and other mineralogic changes related to textural variations imply the physical-chemical conditions of crystallization in the batholith. Because hydrothermal alterations in the quartz monzonite are closely similar to the deuteric ones, the deuteric alterations have some significance to the origin of ore deposits.

The geometrically irregular textural variants and deuteric alterations in the aplite-pegmatites may be the result of increased vapor pressure and of concentration of mineralizers in local, hermetically sealed volumes of rock. This increase led to coarsened grain, recrystallization, to the occurrence of tourmaline and sulfides, and/or to major stability adjustments of mineral composition and crystal structure. Mineral assemblage is systemmatically related to textural type as shown by the progressive decrease of plagioclase and coarsening of grain until only separate bodies of quartz and of K-feldspar rock remain. Chemically deuteric alteration resulted in similar differentiation.

The differentiation pattern of the aplite-pegmatites closely resembles Neuman's hypothetical process of *hydrothermal differentiation*, leading to aplites and pegmatites and also to an aqueous product, possibly rich in ore

[1] Publication authorized by the Director, U. S. Geological Survey.

metals. The similarity of deuteric alteration of aplite-pegmatites to hydrothermal alteration of quartz monzonite and aplite-pegmatites clearly indicates that residual magmatic fluids alone may cause all the observed features of hydrothermal alteration in the quartz monzonites. Theoretically, the migration of residual fluids into volumes of lessened pressure resulting from thermal contraction may cause the observed hydrothermal alterations of the batholith and may also transport ore-metals. These fluids also may gain additional metals released by alteration of the original rock minerals. If hydrothermal alteration releases ore metals from rock minerals, several hundred thousand tons of metal could have been made available to ore solutions from an estimated 5 cubic miles of altered batholithic rock.

These three processes of ore deposition—hydrothermal differentiation, migration of fluids, and alteration release of metals—may be amenable to geochemical-geological testing. Systematic analyses of rocks of varying chemistry and structural positions are proposed as a basis for such tests.

INTRODUCTION

ABUNDANT complex aplite-pegmatite bodies are in the Boulder batholith and locally are associated with ore deposits. A group of these bodies, principally near Basin and Boulder, Mont., exhibit alterations similar to hydrothermal alterations in the wallrocks of the ore deposits. The mineralogic alterations in this group of aplite-pegmatites demand a magmatic origin that implies possible processes of hydrothermal alteration in the vein wallrocks, and which may imply also the source of some ore metals.

The objectives of this report are: (a) to explore the significance of alterations in the aplite-pegmatites to the general problem of hydrothermal alteration associated with the ore deposits of the batholith, and (b) to suggest ways in which the hypothetical significance may be evaluated experimentally. The field relations and petrography of the aplite-pegmatites near Basin and Boulder, Mont., are described briefly and their crystallization history outlined to form a background for discussion of these matters.

All the mineralogic alterations considered herein are generally called hydrothermal. They can be separated into three types which requires a somewhat awkward terminology. *Hydrothermal alteration* is used in both the general sense and as specifically referring to alterations later than the consolidation of the aplite-pegmatites; these later hydrothermal alterations are commonly localized along steep zones of closely spaced fractures, called *alteration zones*. Hydrothermal alterations that are restricted in space to the aplite-pegmatites and that show no spatial relation to structures younger than the aplite-pegmatites are interpreted as and herein called *deuteric alterations*. Uncommonly, the quartz monzonite wallrock of the aplite-pegmatites is hydrothermally altered along the contact between quartz monzonite and aplite-pegmatite intrusive; this hydrothermal alteration that is clearly related to the contact is called *contact hydrothermal alteration*.

Laboratory and field studies of the aplite-pegmatite bodies were pursued intermittently from the summer of 1951 through the summer of 1956. Most attention was given to the aplite-pegmatites near Boulder, Mont.; others were examined only in cursory fashion. Oral reports on some of this work were given before the Geological Society of America meetings at Butte in 1953 (8),

and before the Society of Economic Geologists and the American Institute of Mining and Metallurgical Engineers meetings at New York in 1956 (9).

Sincere thanks are due my many colleagues in the Survey for lively and informative discussions and especially to M. R. Klepper for permission to devote most of my efforts to this problem while associated with the Boulder batholith project. Charles Meyer's advice and interest is gratefully acknowledged. Thanks are due George Mayer, former leasor of the Wendell Phillips claim near Basin, Mont., for his courtesy and help in studying that property. Wayne A. Roberts and Barrie H. Bieler each directed me to two critical occurrences of aplite-pegmatite texture and mineralogy. F. W. Osterwald's criticisms of the manuscript were helpful. This paper is a byproduct of work that was done by the U. S. Geological Survey for the Division of Raw Materials of the U. S. Atomic Energy Commission.

GENERAL GEOLOGIC AND PETROGRAPHIC CHARACTER OF THE APLITE-PEGMATITES

Aplite-pegmatite bodies of simple mineralogy are abundant in the Boulder batholith; the bodies are locally concentrated into dense swarms. The greatest number of aplite-pegmatites comprise a group characterized by complex texture and internal structure. This group occurs wholly within the quartz monzonites of the Boulder batholith. Within this group the size and shape of intrusive bodies and the internal geometrical disposition of the textural types vary between wide limits. This paper describes bodies within the group that exhibit the effects of deuteric alteration (as defined above). These bodies are known only in a strip extending sporadically for about 30 miles from Boulder, Mont., almost to the northern edge of the Boulder batholith.

Wallrocks of the Aplite-Pegmatites.—The rocks of the Boulder batholith range in composition from gabbro to alaskite (6); the most abundant rocks are biotite-hornblende quartz monzonites. These quartz monzonites consist mostly of quartz, K-feldspar, and plagioclase, and variable but generally small amounts of hornblende and/or biotite and/or uncommonly pyroxene. Among the minor accessories, iron oxides and sphene are common, and allanite, apatite, and zircon are generally rare; tourmaline occurs very uncommonly and only in small amounts. The texture is most commonly hypautomorphic, equigranular, locally becoming porphyritic. Crystalloblasts of K-feldspar and less commonly of other minerals are abundant. Other textural varieties were not closely examined.

The Aplite-Pegmatites.—The aplite-pegmatites of the Boulder region occur as small stocks, numerous nearly horizontal tabular bodies, and bodies of irregular shape, ranging in dimensions from a few feet to a few hundred feet. They are especially notable for many pegmatite-like textural variations of grain size and of fabric, which differ in abundance and character. Some of the textural variants are visible in outcrop, but others are microscopic. No evidence of reactions between aplite-pegmatite and quartz monzonite wallrock was noted in the Boulder region except for rare hydrothermal alteration of quartz monzonite along contacts; in contrast, contact effects are common among related aplite-pegmatites near Butte.

The aplite-pegmatites contain about one-third quartz, about one-third to one-half K-feldspar, slightly lesser amounts of sodic oligoclase to albite, minor amounts of biotite and tourmaline, and trace amounts of apatite, chalcopyrite, fluorite, magnetite, molybdenite, pyrite, and zircon. Alteration minerals are chlorite, dickite-kaolinite, epidote, hematite, hydromica, leucoxene, limonite, rutile, sanidine (?), sericite, and an unidentified clay. Most of the aplite-pegmatites are leucogranite in the Johannsen classification; others are alaskite, granite, and/or quartz monzonite.

The aplite-pegmatites are chiefly fine- to medium-grained xenomorphic to subhypautomorphic in texture, and consist primarily of an even-grained mosaic of quartz and K-feldspar and lesser amounts of zoned plagioclase crystals and scattered small biotite anhedrons. The average grain size ranges from 0.5 mm to 2 mm but is most commonly 0.75 mm.

Although many intrusives look homogeneous, internal variation of texture and grain size is common on all scales. Systematic variations in mineral composition are related to this internal variation. Commonly larger bodies are coarser grained and also seem to contain slightly more biotite than smaller ones. In addition, grain size of the aplitic texture varies slightly within individual intrusives as shown by irregular wisps and large volumes of finer-grained rock set within otherwise uniform and coarser-grained rocks. Other microscopic textural variants are cauliflower-like volumes of granophyric quartz slightly coarser than and superimposed on the xenomorphic texture of the aplite. Quartz granophyres seem to occupy vaguely defined and irregular volumes, possibly localized by joints, within intrusives, and the amount varies greatly. Micro-myrmekite is uncommon and its structural distribution is undetermined.

The best documented textures are pegmatitic; their structural distribution and abundance vary radically from body to body, even among those that are only a few feet apart. Some intrusives contain only a few scattered pegmatites, others are almost completely pegmatite. The geometrical disposition of pegmatites within intrusives varies widely and generally shows no relation to the shape or size of the bodies.

Coarse-grained xenomorphic intergrowths of quartz and K-feldspar, with subordinate plagioclase, and commonly with appreciable amounts of tourmaline are the most abundant pegmatitic-textured rocks in the aplite-pegmatites. This xenomorphic type of pegmatite also occurs as thin tabular lenses, locally anastamosing and younger than the microscopic variations in texture. These intergrowths average about 1 inch in grain size but vary greatly. Small irregular pods, generally less than 6 inches in maximum dimensions, are the commonest pegmatites. Some of these pegmatites are sharply bounded and contrast markedly in grain size with their matrix, but others show a gradation in grain size into the matrix and are ill-defined. Miarolitic cavities, large quartz aggregates, and clusters of tourmaline are common in the central parts of both types of xenomorphic pegmatites and muscovite and/or sulfides appear locally.

Graphic granite showing uncommonly irregular quartz glyphs, is almost as abundant as the xenomorphic pegmatites. It consists of quartz and K-

feldspar, and variable but small amounts of plagioclase. Graphic granite commonly occurs with the xenomorphic pegmatite, either as zones along one or both sides of pegmatite lenses or as small satellitic pods. It also occurs completely apart from other textural variants of the aplite-pegmatites, almost entirely as thin tabular volumes that commonly parallel the walls of the intrusive. Isolated, small pods of graphic granite in even-grained aplite are known but are uncommon. Thin interstitial films of tourmaline occur rarely in the graphic granite.

Related to the xenomorphic and graphic pegmatitic textures are isolated, one- to three-inch euhedrons of graphic textured K-feldspar, or K-feldspar, with or without large anhedral, milky white quartz crystals. A few of the K-feldspar crystals have miarolitic cavities along their boundaries. Isolated and grouped tourmaline poikiloblasts in the normal aplitic fabric are distributed as erratically as the small pods of xenomorphic pegmatite.

Isolated large quartz pods and large K-feldspar pods, with or without pegmatite-textured rims, are few but noteworthy. They are not associated with other textural variants in any evident manner. These pods comprise appreciable fractions of the intrusives in which they occur and have dimensions of several inches to several tens of feet. They occur in aplite-pegmatite bodies, whose shape they mimic, and as isolated stock-like bodies in quartz monzonite. The quartz pods are coarse to huge grained, commonly vuggy, and milky white in color; they occur both in bodies of even and of irregular texture. The K-feldspar pods were seen in only three places: (a) as an isolated pure K-feldspar stock, about 75 feet by 50 feet in plan, (b) as a small pod bordering coarse pegmatite-textured rock centrally located in a tabular aplite-pegmatite body, and (c) as a partial rim on a large quartz mass. The K-feldspar (sanidine?) rock of the pods is medium- to coarse-grained, pervasively miarolitic on a small scale, and contains besides K-feldspar only minor amounts of dickite-kaolinite, muscovite, quartz, and rutile; the K-feldspar rock is everywhere deuterically altered.

MINERAL ALTERATIONS

In the region around Boulder and Basin and northward toward the edge of the Boulder batholith, the quartz monzonite contains numerous east- and northeast-trending, nearly vertical, thin alteration zones (2), in part containing veins of silica and locally small amounts of barite, precious metals, sulfides, and uranium minerals. Alteration of the quartz monzonite along these zones, as observed in thin sections, consists of (a) replacement of plagioclase and in very small part of K-feldspar by dickite-kaolinite, (b) transformation of biotite to hydromica and rutile, and hornblende to epidote, (c) intense strain-shadowing in quartz, (d) in many places recrystallization of the original slightly perthitic K-feldspar to a limpid, sanidine-like K-feldspar, and (e) recrystallization of quartz to a fine-grained mosaic. The most intense alterations resulted in sericite, principally at the expense of K-feldspar, but also from plagioclase or from its kaolinitic alteration product. The alteration of the aplite-pegmatites along these zones is identical in character but differs in proportions of alteration products.

A clear spatial progression of mineralogic changes reflects an increasing intensity of hydrothermal alteration in toward veins or central parts of alteration zones. Whitening of plagioclase due to the alteration to dickite-kaolinite appears first, followed by the alteration of biotite to hydromica and rutile and of hornblende to epidote. The next change is the alteration of K-feldspar, either to a recrystallized K-feldspar, thence to sericite, or directly to sericite. Increasing sericitization and the appearance of quartz-kaolinite and quartz veinlets mark the next stage, followed, in some alteration zones, by quartz veins in a matrix of sericite alone.

These alterations are confined to zones of close-spaced fracturing that postdate consolidation of the aplite-pegmatites, but similar alterations in the aplite-pegmatites are confined solely to these intrusives and are not controlled by structural features younger than the intrusives. These alterations of the aplite-pegmatites consist of small to large parts of an intrusive wherein plagioclase is altered to kaolinite-dickite, biotite to hydromica and rutile, apatite possibly added and, uncommonly, K-feldspar altered, if at all, to a limpid, sanidine-like K-feldspar. The alteration products are the same as those in the younger alteration zones transgressing both aplite-pegmatite and quartz monzonite.

The altered rock in the aplite-pegmatites is disposed in the same manner as the textural variants of the aplite-pegmatites, and the alterations commonly coincide with these textures. Rare sericite coatings on internal joints in the aplite-pegmatite bodies and thin, discontinuous, and rare selvages of hydrothermal alteration of quartz monzonite along the contacts of some larger aplite-pegmatite bodies are related features. These alterations, so evidently confined to the aplite-pegmatites, are probably deuteric.

The deuteric and hydrothermal alterations of the aplite-pegmatites and of the quartz monzonites are chemically similar; hence, they were probably caused by similar processes. Differences in the proportions of alteration products reflect initial differences in mineralogic composition between aplite-pegmatite and quartz monzonite. Also, hydrothermal alteration along the alteration zones in quartz monzonite was stronger and more widespread because it commonly produced more sericite and quartz veining than did deuteric alteration. These differences do not suggest any differences of chemical reactions or of chemical composition of the altering solutions. Concentrations of ore minerals along some of the hydrothermal alteration zones do not occur in deuterically altered aplite-pegmatite; this difference, however, does not necessarily imply a chemical difference between the two altering solutions, for reasons indicated below.

The mineralogic changes evident in hydrothermal alteration of the quartz monzonite and in deuteric alteration of the aplite-pegmatites are due principally to loss of sodium and calcium along with the loss of varying amounts of iron and magnesium (14, 16).

PETROLOGY OF THE APLITE-PEGMATITES

The origin of the contrasting textures and of deuteric alteration and the differentiation of the aplite-pegmatites is significant to ore deposition. The

contrasting textures bear particularly on the physical-chemical conditions that led to deuteric alteration; the deuteric alteration, in turn, because of its chemical similarity to hydrothermal alteration, must be related to the physical-chemical conditions of hydrothermal alteration. The further differentiation of the aplite-pegmatites, which are the last products of the main trend of differentiation in the batholith, is presumably an intermediate process between the crystallization of the main parts of the batholith and the ultimate deposition of ore.

Origin of the Contrasting Textures of the Aplite-Pegmatites.—The grain size, fabric, and mineralogy of the different parts of aplite-pegmatite bodies are mainly a function of the vapor pressure of water at the time of crystallization of each part, and the deuteric alterations, the tourmaline, and the crystalloblastic textures, such as granophyric quartz, are a further reflection of local concentrations of water, phosphorus, sulfur, and boron.

The textural variants of the aplite-pegmatites in the Boulder-Basin region do not extend out of the aplite-pegmatite intrusives, and they show no evidence in their geometrical disposition of any control by the wallrocks, nor are they in any way reflected in the wallrock. The occurrences of deuteric alterations and of tourmaline are similar to those of the textural variants. Therefore, the origin of these features must be assigned to the crystallization of the aplite-pegmatites from their magma rather than to some later event. The differences between intrusives indicates slight differences in their crystallization.

The grain size of most of the aplite-pegmatite is commensurate with that of its quartz monzonite wallrocks. The lack of chilled borders indicates that the aplites were intruded into warm wallrocks, such that the temperatures of crystallization of the aplite-pegmatites must not have been much less than the final temperatures of crystallization of the quartz monzonite wallrocks. The grain size of aplite is commonly accepted (e.g., 15, p. 163) to imply a "dry magma." The aplites, however, are not significantly finer grained than the quartz monzonites. A dry magma of the composition of the quartz monzonite, because of its complex composition, should presumably have a lower temperature of crystallization than a dry magma of the much simpler aplite-pegmatite composition. This theoretical temperature contrast is incompatible with the observed age relations of the two rocks.

An increase in the concentration of mineralizers, principally water, relative to the earlier quartz monzonites should on experimental grounds (3) serve to lower materially the temperature of crystallization. Furthermore, the higher the concentration of mineralizers, the lesser the viscosity of a silicate melt, a factor that should decrease the rate of crystal nucleation while increasing the rate of crystal growth and promoting coarser grain size (4). With the approach of final consolidation, water vapor pressure increases rapidly and water becomes an efficient mineralizer. As the rock cools, early formed minerals become unstable, and, if the water of the magma has not yet escaped and its vapor pressure is high, the first crystallized minerals are changed into new species stable at the lower temperatures of final consolidation (3, p. 508–509). Thus the aplite magmas must have contained a higher concentration of water and other mineralizers than the parent quartz monzonitic rock.

The pegmatitic textures, coarser grain, quartz granophyre, tourmaline, and deuteric alteration in the aplite-pegmatites may have originated in the following way. The aplite-pegmatite bodies crystallized largely as a whole—rather than from the borders inward—and large irregular volumes solidified before the rest of the body in such a manner that volumes of incompletely crystallized aplite-pegmatite magma were locally isolated and more or less hermetically sealed for a time. In such isolated volumes, the enclosed water was effectively trapped so that the water vapor pressure increased as crystallization continued. Depending on the time of sealing or its degree of effectiveness and on the composition of the mineralizers trapped in the sealed volume, there resulted: (a) an increase in the grain size—beyond that of the bulk aplite of these intrusives—and textural complexities of the crystallizing feldspars and quartz, with or without the crystallization of tourmaline and/or sulfides; or (b) recrystallization of quartz into granophyric intergrowths replacing the feldspars; or (c) deuteric alteration of plagioclase to dickite-kaolinite and biotite to hydromica and rutile; or finally (d) some combination of these effects.

Evidence for local concentrations of mineralizers during crystallization of the aplite-pegmatites are (a) the miarolitic cavities in pegmatite-textured rock, locally containing sulfides, (b) the greater extent of subsolidus unmixing in feldspars of pegmatitic textured volumes, (c) the sporadic and highly localized tourmalines, and (d) the greater abundance of apatite in deuterically altered parts of the aplite-pegmatites. The indiscriminate occurrence of tourmaline in single intrusives in pegmatitic volumes, in small, slightly coarsened non-pegmatitic volumes, and in the common fine- to medium-grained aplites indicates that the mineralizers were hermetically sealed in at different times during crystallization.

A few intrusives around Boulder that contain the most textural variants, tourmaline, and deuteric alterations are those partly surrounded by thin quartz monzonite selvages in which plagioclase is altered to dickite-kaolinite and biotite to hydromica and rutile. Water and other mineralizers escaped freely during the course of crystallization from those aplite-pegmatites free or nearly free of textural variants, deuteric alterations, and tourmaline and from those of fine and even grain.

Differentiation of the Aplite-Pegmatites.—The aplite-pegmatites as a group are one product of differentiation of the Boulder batholith. They were further differentiated by two processes: (a) crystal-liquid fractionation and (b) deuteric alteration. The products of this differentiation are coarsening of texture of quartz-feldspar fabrics, accompanied by progressive elimination of sodium and calcium. The sequence of differentiation progressed much as follows. Coarsening of grain was followed by the segregation of quartz and K-feldspar, and a decrease of plagioclase, into fairly pure if small pegmatites. The next step is represented by graphic textured quartz and K-feldspar that are transitional into large discrete quartz and nongraphic K-feldspar crystals in even-grained aplite. Next, separate pods of quartz or of K-feldspar, enclosed in separate aplite-pegmatite intrusives were formed. Ultimately, the separation continued to the formation of distinct bodies of quartz or of K-feldspar, occurring apart from aplite-pegmatite. Plagioclase was progres-

sively eliminated until it was virtually absent. Biotite and the minor accessories continued into the K-feldspar end-stage, but they and K-feldspar became nearly absent from the quartz end-stage.

The chemical changes resulting from deuteric alteration in the aplite-pegmatites—and from hydrothermal alteration of the quartz monzonite—led to similar differentiation products. As a result of deuteric alteration, sodium, calcium iron, and magnesium were effectively removed from the rock. The remainder is K-feldspar and quartz with kaolinite-dickite, which last is the major difference from the products of crystal-liquid differentiation. Separate masses of quartz and K-feldspar were not formed in this process. However, the separate aggregates of vein quartz and of sericite as an extreme product of the hydrothermal alteration of the quartz monzonite are analogous to the quartz pods and K-feldspar pods in the aplite-pegmatite sequence of crystal-liquid differentiation. Water in some unknown way may have effected the separation of sodium and calcium from potassium in the crystallization and alteration processes of differentiation of the aplite-pegmatites.

SIGNIFICANCE OF THE APLITE-PEGMATITES TO ORE DEPOSITION

The crystallization history of the aplite-pegmatites in the Boulder region suggests that chemical processes, active during the end stages of crystallization and during subsequent cooling of the Boulder batholith, may be significant to the ore deposition. Certain ore-forming processes are considered here simply to explore them briefly and where feasible to indicate ways in which they might be tested.

The aplite-pegmatite magmas might have directly contributed metals to ore deposits by two principal processes: (a) by way of differentiation of liquids during crystallization; and (b) as a result of metal abstraction and migration during deuteric and/or hydrothermal alteration.

The hypothetical process of hydrothermal differentiation in late magmatic stages (12) would give rise to siliceous magmas, crystallizing as aplites and pegmatites, and to aqueous magmas or watery solutions enriched in precious metals and base metal sulfides. The end-stage differentiation of the aplites into a K-feldspar-rich phase and a quartz-rich phase may be an example of Neumann's hydrothermal differentiation. This hypothetical ore-forming process may be tested at least in part. Granted that the known quartz differentiates of the aplite-pegmatites are not now ore, they may have been left behind during movement of the metal-enriched aqueous solutions. If so, the base metal content of the quartz-rich differentiate should be enriched relative to the parent aplite-pegmatite, while that of the K-feldspar differentiate might be somewhat depleted. Analyses of the minor elements of the aplite-pegmatites and their differentiates might show a pattern of ore-metal partition and enrichment in the direction of the quartz differentiates. Single minerals, preferably the same species, rather than rock samples of varying mineralogic composition from the aplite-pegmatites and their textural variants, from the quartz pods, and from the K-feldspar pods should be tested to avoid those differences due to varying crystal-chemical properties of the rock-forming minerals and those due to their differing proportions.

Deuteric alteration of the aplite-pegmatites also may have concentrated or supplied ore metals to migrating solutions. Rock minerals generally contain a few grams of various metals per ton of rock. The altered minerals of the aplite-pegmatites, principally plagioclase and biotite, may have contained minor elements by solid solution, adsorption, and physical entrapment. Recrystallization and reconstitution of minerals (during deuteric or other alteration) should in general expel foreign minor elements. If the newly formed minerals do not strongly adsorb or otherwise recapture these elements, they may remain in the solutions, be carried away and perhaps deposited in economic concentrations. Testing this suggested process of ore deposition should be simple. Minor element analyses of unaltered and of equivalent deuterically altered aplite-pegmatite should give an indication, if not a positive answer.

The derivation of ore-metal by deuteric alteration of the aplite-pegmatites is not directly promising because the volume of altered rock is small. A metal concentration of a few grams per ton parlays into tens and hundreds of thousands of tons of metal only when cubic miles of rock are considered. When such large volumes of rocks are altered, release of ore metals to solution is important. The volume of hydrothermally altered quartz monzonite in the Boulder batholith is huge and may be large relative to similar batholiths. The recent map (2) of part of the region around and north of Basin and Boulder demonstrate the large areal extent of alteration zones, and these are only a fraction of the altered zones actually present in outcrop, but not individually mappable. At least 5 cubic miles of altered rock exists to a depth of one mile in the nearly 2,000 square miles of exposed batholith. The release of even a few grams of metal per ton of rock to the solutions would have supplied several hundred thousand metric tons of metal for ore deposition.

The chemical similarity of hydrothermally altered quartz monzonite with deuterically altered aplite-pegmatite is evidence that the composition of the altering solutions need not differ from that of the residual fluid phase in the crystallized magma. With this observation as a starting point, hydrothermal alteration and ore deposition in the Boulder batholith may be postulated to have proceeded in the ways outlined below.

The hypotheses proposed here may be explained by assuming that an igneous body must continually contract its volume during its entire cooling history. This contraction first results in joints and fractures, which provide sites for aplite and pegmatite bodies within the intrusive (1, p. 29–31). Further contraction results in more joints and fractures, and in an increase in the permeability of the rock resulting from fine fractures and loosening of grain boundaries. The openings may be filled not only by fluids migrating from the cooling rock mass, but also by intrusion of other igneous rocks.

Once thermal contraction, still at moderately high temperatures late in the cooling history of the batholith, becomes accelerated so that the fabric is loosened, migration of the residual fluids in and from the fabric can become appreciable under the prevailing hydrodynamic gradient. With the fluids go many materials that remained in solution, including the ore metals and the anions that appear in the ore and gangue minerals of ore deposits.

These residual fluids also transfer heat to the fractures and joints. Al-

though the amount of heat energy thus transferred is no doubt small, it interrupts temporarily the decrease in rock temperature near openings to which the fluids moved, especially if the fluids temporarily are held in and near the opening. If some or all the minerals had cooled to temperatures below their fields of stability and became metastable, the interruption of cooling could well have catalyzed production of a more stable assemblage. This process, in conjunction with the general property of water to promote chemical reactions, could bring about the late stage hydrothermal alterations in the Boulder batholith. The migrating fluids must be impounded in the openings sufficiently long to transfer heat from the residual fluids to the rock that they touch before the rock can be hydrothermally altered along such structure.

These residual fluids furthermore, during the alterations they effected may have released metals from the primary rock minerals that might be added to the "ore solutions." The altered rock thus could have supplied many hundreds of thousands of tons of metals. The great number of alteration zones (potential vein structures) of large size, most of which are free of any metal concentrations, may be a major source for the local economic concentrations of metals in some of the alteration zones (vein structures).

At present the suggested hypothesis seems theoretically logical, but some parts need to be tested. A loss of metals from the quartz monzonite magma needs to be demonstrated, but the problem of demonstrating significant loss of metals from the unaltered quartz monzonite is more readily approached. If the proposed process operated, the pristine quartz monzonite must have had higher ore-metal concentrations than the unaltered rock, as well as the hydrothermally altered rock, which can now be sampled. Should it be possible to find decreasing gradients in ore metal concentrations in the quartz monzonite toward alteration zones, an originally higher metal content in the pristine quartz monzonite would be suggested, resulting from wallrock alteration as outlined above. Further, systematic contrasting of the metal contents of altered and unaltered rock equivalents would determine if metals had been dissolved and removed by the altering fluids.

Alteration release of elements as a factor in providing the elements to form other minerals and ore deposits is implied by much of the petrologic and economic geology literature, particularly in connection with studies of metamorphism. The subject has received some theoretical attention, notably in DeVore's (5) studies of element redistribution during recrystallization. Pecora (13) noted the role of alteration release in providing elements for utilization in the formation of stable, secondary minerals in some Montana pegmatites. Mackin (7) explicitly invoked and documented deuteric alteration release as a major factor in supplying iron for the ore deposits of the Iron Springs district of Utah.

Most of the published data and comment regarding alteration of minerals as a source of elements to be incorporated in other minerals refers to the essential major elements of the altering mineral. Alteration release of the minor elements of minerals has received some published consideration, as in the paper by DeVore (5), but I have found no published satisfactory documentation of alteration release of minor base metals from rock minerals. For reason of the sluggish stability adjustments characteristic of most alteration reactions accom-

panying falling temperature and because of the apparent large tolerance of low temperature minerals for a large variety and relatively large quantity of nonessential elements, alteration release of minor elements needs more careful study and experimentation than it has yet received.

For two reasons the rock specimens should be analyzed in such a way that the fabric mode of distribution of the metals under consideration may be partially determined (10). Not only the total content of each metal in each specimen, but also its quantitative distribution between two modes of occurrence should be determined: (a) metals contained, by whatever manner, in rock mineral structures; and (b) *labile metals* (11), which are those that occur as discrete metal compounds, such as chalcopyrite and uraninite, as cations or anions adsorbed on the surfaces of crystal discontinuities, and dissolved in rock fluids. The quantity of labile metal is a measure of that amount potentially available for transfer in residual fluids. Thus a concentration gradient of labile metal may be a more reliable indicator of transfer by residual fluids than a total metal concentration gradient. Similar measurements of labile metal concentrations in altered rock would determine the degree of minor element expulsion due to alteration.

The exact analytical details for determination of labile metals remain to be worked out. A general analytical approach has been worked out by John C. Antweiler and the author. It involves leaching of rock samples in various strengths and combinations of hydrogen peroxide and ammonium carbonate. These reagents effectively dissolve base metal compounds without dissolving any appreciable fraction of the common igneous rock minerals.

In conclusion, the interpretations and hypotheses presented here are considered only as possibilities, which may be of interest because they may be tested by geochemical techniques and because they may bear importantly on means and philosophies of prospecting batholiths.

U. S. Geological Survey,
Denver, Colorado,
Nov. 25, 1957

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IDENTIFICATION TABLES FOR URANIUM AND THORIUM MINERALS

A. VOLBORTH

URANIUM and thorium minerals, taken together, probably have received more attention during recent years than any other group or category of minerals. D'Arcy's Mineralogy of Uranium and Thorium Bearing Minerals (4), though published less than a decade ago, already is incomplete because of rapid advancements in studies of such minerals. The comprehensive work on the mineralogy of uranium and thorium, known to be in preparation by the U. S. Geological Survey (8), is therefore being awaited with considerable interest.

In 1956 the present writer completed a study of uranium, thorium, zirconium, lithium, and beryllium minerals. The results of this work, together with suggestions for prospecting, are being published in Finland (27). While the manuscript for this book was being prepared, it became obvious that the collected data could be presented in the form of a new type of identification table for uranium- and thorium-bearing minerals based on color, fluorescence, specific gravity, composition, and other pertinent properties. The tabulation, which appears on the following pages, is offered as an aid in recognizing and determining these minerals—all too often a difficult matter.

The data concerning fluorescence are based mainly on the studies of Bültemann (3), Haberlandt, Hernegger, and Scheminzky (10a), Kirchheimer (14), and Meixner (16). Additional information relating to fluorescence and other physical properties of recently discovered or redescribed minerals has been compiled from papers and reports of Axelrod, Grimaldi, Milton, and Murata (1), Bowie and Horne (2), C. Frondel (5, 6), C. Frondel and Meyrowitz (7), J. W. Frondel and Cuttitta (10), J. W. Frondel (9), Hewett, Stone, and Levine (11), Horne (12), Hutton (13), Milne and Nuffield (17), Mrose (18), Nuffield and Milne (19), Pabst (20, 21), Stern, Stieff, Girhard, and Meyrowitz (22), Stieff, Stern, and Sherwood (23), Thompson, Ingram, and Gross (24), Thompson, Weeks, and Sherwood (25), and Vaes and Kerr (26).

The chief purpose of the table is to make it possible for a field investigator quickly to assign an unknown radioactive mineral to a certain mineral group. The composition of each known mineral is included, as this often enables one to effect an identification by means of a simple chemical test, or at least to reduce the number of possibilities within a given group. The table also may prove to be helpful for rapid identification in the laboratory.

The minerals are arranged first into five groups according to their general color: black, dark brown, or brown minerals; yellow minerals; green minerals; red or orange minerals, and colorless minerals. It is recognized that color generally is not a distinctive property of a mineral; nevertheless, among the

IDENTIFICATION TABLE FOR URANIUM AND THORIUM MINERALS

A. Volborth

Mackay School of Mines, University of Nevada, 1957

COLOR Fluorescence	2537AU	3660AU	Fluorescence Color	Sp. Gr.	Mineral Name	Chemical Composition	Remarks on Color Variations, Habit, etc.
	1	1					
Fluorescent	3	?	orange red	4.8-3.9	Zircon	$ZrSiO_4$	rdsh brwn, colorless, ylw, gray, grn; prismatic, pyramidal
BLACK, DARK BROWN OR BROWN MINERALS Non-fluorescent	-	-		10.5-8	Uraninite	UO_2	also grnsh black; cubes
	-	-		9.7-8	Thorianite	$(Th, U)O_2$	also brwnsh black; cubes
	-	-		9-6	Pitchblende	(UO_2, UO_3)	also grnsh black; reniform
	-	-		8-5.2	Tantalite-Columbite	$(Fe, Mn)(Ta, Nb)_2O_6$-$(Fe, Mn)(Nb, Ta)_2O_6$	Ta.-prism. column. striated, Co.-tabular
	-	-		6.4	Clarkeite	$(Na, K, Ca, Pb)_2U_2O_7 \cdot nH_2O$	also orange or ylwsh; massive
	-	-		6.4-4.2	Microlite-Pyrochlore	$(Na,Ca)_2(Ta,Nb)_2O_6(OH,F)$-$(Na,Ca)Nb_2O_6F$	dark brwn, ylwsh, rdsh; octahedrons, cubes, grains
	-	-		6.2-4	Fergusonite	$(Y,Er,Ce,Fe)(Nb,Ta,Ti)O_4$	also ylw surface; prism., pyramidal, grains
	-	-		6-4	Samarskite	$(Y,Er,Ce,U,Ca,Fe,Pb,Th)(Nb,Ta,Ti,Sn)_2O_6$	also brwn, ylwsh brwn; waxy, massive
	-	-		5.8-4	Polycrase-Euxenite	$(Y, Ca, Ce, U, Th)(Ti, Nb, Ta)_2O_6$	occ. grnsh, brwnsh tint; prism. or tab.
	-	-		5.5-4.6	Monazite	$(Ce, La, Y, Th)PO_4$	brwn, pale ylw, honey ylw; flat prisms
	-	-		5.4-4.5	Brannerite	$(U, Ca, Fe, Th, Y)_3Ti_5O_{16}$?	also olive grn surf.; prismatic, long prisms, nodules
	-	-		5.4-4.5	Thorite-Orangite	$Th\ Si\ O_4$	also orange ylw; zircon habit
	-	-		5.3-3.8	Betafite	$(U, Ca)(Nb, Ta, Ti)_3O_9 \cdot nH_2O$	often grnsh brwn or ylw; octahedral, large crystals
	-	-		5.1-4.4	Xenotime	$Y\ PO_4$	ylwsh or rdsh brwn, gray, ylw, grnsh; zircon habit
	-	-		5	Coffinite	$U(SiO_4)_{1-x} \cdot (OH)_{4x}$	cryptocrystalline, amorph.
	-	-		5-4.3	Zirkelite	$(Ca, Fe, Th, U, Y)_2(Ti, Zr)_2O_5$?	flattened octahedra, rare
	(3)	-		4.8-3.9	Zircon	$ZrSiO_4$	see above
	-	-		5.1-3.6	Wiikite	U-bearing samarsk. and eux.-like min.	also ylwsh; waxy, massive
	-	-		4.7-4	Gadolinite	$FeY_2Be_2Si_2O_{10}$	also grnsh blk, brwn, crystals rare, prism.
	-	-		4.7	Delorenzite	$(U, Fe, V)(Ti, Sn)_3O_8$	rhombic, elongated, tabular crystals, rare
	-	-		4.6-3.3	Ampangabeite	$(U,Y,Er,Th,Ca)_2(Nb,Ta,Fe,Ti)_7O_{18}$?	also ylw brwn; rounded, rad. prism. aggreg., rare
	-	-		4.5	Davidite	$(Fe^{+2}\ U, Ca, Zr, Th, Ce)(Ti, Fe, {}^{+3}V, Cr)_3(O,OH)_7$?	large crystals
	-	-		4.2-2.7	Allanite, Orthite	$(Ca,Fe,La)_2(Al,Fe,Mg)_3(OH)(SiO_4)_3$	also grnsh or brwnsh; tabular, massive
	-	-		?	Ianthinite	hydrated oxide of U^{+4}	dark violet; rhombic crystals, rare
	-	-		?	Rauvite	$CaO \cdot 2UO_3 \cdot 2V_2O_5 \cdot 16H_2O$?	purple red or dark blue earthy masses, rare

FIG. 1.

YELLOW MINERALS
Fluorescent Minerals

		strongly fluorescent				
3	2	yellow-green	4.8 ?	Rutherfordine	$(UO_2)CO_3$	fibrous coatings on pitchblende, rare
2	3	yellowish-green	4.6	Schoepite	$2UO_3 \cdot 5H_2O$	pale grnsh ylw; plates, rare
3	3	yellow-green	4.1-3.5	Meta-uranocircite	$Ba(UO_2)_2(PO_4)_2 \cdot 8H_2O$	also greenish; micaceous, like autunite, rare
3	2	yellow-green	4-3.7	Uranopilite	$(UO_2)_6(SO_4)(OH)_{10} \cdot 12H_2O$	ylwsh green; fibrous coat. on pitchblende
2	1	pale yellowish	3.9-3.8	Uranophane, U-til	$Ca(UO_2)_2(SiO_3)_2 \cdot (OH)_2 \cdot 5H_2O$	fibrous, massive, rad. aggreg.
2	1	yellowish, occ.	3.5	Zippeite	$2UO_3 \cdot SO_3 \cdot 5H_2O$?	orange-ylw; fibrous, crusts, aggreg.
3	3	yellow-green	3.5-3.4	Uranospinite	$Ca(UO_2)_2(AsO_4)_2 \cdot 8\text{-}10H_2O$	grnsh ylw, pale ylw; micaceous, rare
2	3	lemon yellow	3.2	Sabugalite	$HAl(UO_2)_4(PO_4)_4 \cdot 16H_2O$	ylw flrcence 3660AU; like autunite, rare
3	3	yellow-green	3.2-3.0	Meta-aut.,Autunite	$Ca(UO_2)_2(PO_4)_2 \cdot 6\text{-}12H_2O$	micaceous, lamellar crystals
3	3	green	2.5	Schroeckingerite	$NaCa_3(UO_2)(CO_3)_3(SO_4) \cdot F \cdot 10H_2O$	grnsh ylw; micaceous, glob. aggreg.
3	3	apple green	2.4	Liebigite	$Ca_2(UO_2)(CO_3)_3 \cdot 10H_2O$	grnsh ylw; gran. scaly aggreg.
		weakly and medium fluorescent				
-1	-1	dull brownish	6.4-3.9	"Gummite"	Mixt. of U-min., some flrcent	gum-like
1	1-2	yellowish green	5.4-5.3	Billiétite	$BaO \cdot 6UO_3 \cdot 11H_2O$	platy, rare
-	1	orange-brown	4.6	Soddyite	$(UO_2)_5(SiO_4)_2(OH)_2 \cdot 5H_2O$	also grnsh ylw; minute prismatic crystals, rare
1	1	pale ylwsh,2537AU	4	Beta-uranophane	$Ca(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$	grnsh fluorescence 3660AU; fibrous
-	-1	brownish green	4	Renardite	$Pb(UO_2)_4(PO_4)_2(OH)_4 \cdot 7H_2O$	platy, rare
-1	-1	greenish, occ.	4-3.5	Carnotite	$K_2(UO_2)_2(VO_4)_2 \cdot 1\text{-}3H_2O$	fine granular, rhombic crystals
-	1	dull ylwsh orange	3.8-3.5	Sklodowskite	$Mg(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$	minute rhombic prisms, rare
1-2	1-2	yellow-green	3.7-3.3	Abernathyite	$K(UO_2)(AsO_4) \cdot 4H_2O$	tabular crystals, rare
-	-1	yellowish brown	3.5	Epi-ianthinite	$UO_3 \cdot 2H_2O$?	alteration prod. of Ianthinite, rare
?	?	yellow-green ?	3.3	Sharpite	$(UO_2)CO_3 \cdot H_2O$?	greenish yellow; fibrous crusts, rare
1	1	orange-brown	3.3	Phosphuranylite	$Ca(UO_2)_4(PO_4)_2(OH)_4 \cdot 7H_2O$	pulverulent coatings, monocl. leaves, rare
1-2	1	yellowish green	3.3	Salécite	$Mg(UO_2)_2(PO_4)_2 \cdot 8\text{-}10H_2O$	micaceous, like autunite, rare
1	2	green	3.3	Novačekite	$Mg(UO_2)_2(AsO_4)_2 \cdot 8\text{-}10H_2O$	straw yellow; platy, rare
1	1	yellow-greenish	2.1	Bayleyite	$Mg_2(UO_2)(CO_3)_3 \cdot 18H_2O$	prismatic, rare

FIG. 2.

YELLOW MINERALS
Non-Fluorescent Minerals

-	7.3–7.1	Curite	$3Pb0 \cdot 8U0_3 \cdot 4H_20$	orange-yellow; acicular
-	7–6	Kasolite	$Pb(U0_2)(Si0_3)(0H)_2$	brown-yellow; prismatic, rare
-	6.7–5.8	Walpurgite	$Bi_4(U0_2)(As0_4)_20_4 \cdot 3H_20$?	straw yellow; tabular, aggreg. and rad. groups, rare
-	6.4–3.9	"Gummite"	Mixt. of U-min., some fireent	gum-like
-	6.4	Uranospherite	$(Bi0)(U0_2)(0H)_3$?	orange-yellow, brick red; hemispheres, rare
(1)	6	Soddyite	$(U0_2)_5(Si0_4)_2(0H)_2 \cdot 5H_20$	minute pyramidal crystals, rare
-	5.4	Parsonsite	$Pb_2(U0_2)(P0_4)_2 \cdot 2H_20$	pale yellow-brown; tabularcrystals, rare
-	5.2	Becquerelite	$7U0_3 \cdot 11H_20$	also orange-yellow; tabular
-	5	Dumontite	$Pb_2(U0_2)_3(P0_4)_2(0H)_4 \cdot 3H_20$	weak brwnsh grn fire once 3250–3750AU, rare
(-1)	4.	Renardite	$Pb(U0_2)_4(P0_4)_2(0H)_4 \cdot 7H_20$	tabular, rare
(-1)	4–3.5	Carnotite	$K_2(U0_2)_2(V0_4)_2 \cdot 1–3H_20$	occ. grn-ylw; powder, aggreg., crusts
-	3.9–3.8	Metatyuyamunite	$Ca(U0_2)_2(V0_4)_2 \cdot 3–5H_20$	canary ylw, grnsh ylw; micaceous
-	3.6–3.3	Tyuyamunite	$Ca(U0_2)_2(V0_4)_2 \cdot 5–8.5H_20$	pale or grnsh ylw; micaceous, pulverulent
-	3.5	Epi-lanthinite	$U0_3 \cdot 2H_20$?	alteration prod. of lanthinite, rare
(-1)	3.5	Cuprosklodowskite	$Cu(U0_2)_2(Si0_3)_2(0H)_2 \cdot 5H_20$	pale grn-ylw; minute rhombic prisms, rare
-	3.5	Sklodowskite	$Mg(U0_2)_2(Si0_3)_2(0H)_2 \cdot 5H_20$	lemon ylw; minute rhombic prisms, rare
(1)	3.3	Ferghanite	$U_2(V0_4)_2 \cdot 6H_20$	pale yellow, sulphur yellow; scales, rare
-	3.3	Troegerite	$H_2(U0_2)_2(As0_4)_2 \cdot 8H_20$?	pale yellow; tabular, crystals gypsum-like, rare
-	3.1	Bassetite	$Fe(U0_2)_2(P0_4)_2 \cdot 8H_20$	thin tablets, fan-like groupings, rare
-	?	Uvanite	$U_2V_60_{21} \cdot 15H_20$?	brwnsh ylw, rare
-	?	Umohoite	$(U0_2)Mo0_4 \cdot 4H_20$?	cryst masses and coatings, rare
-	?	Vandendriesscheite	$Pb0 \cdot 7U0_3 \cdot 12H_20$?	also orange-brown, or reddish, rare

FIG. 3.

GREEN MINERALS

Fluorescent Minerals			strongly fluorescent			
	3	3	yellow-green	4.1-3.5	Meta-uranocircite	$Ba(UO_2)_2(PO_4)_2 \cdot 8H_2O$	also yellow; micaceous, like autunite, rare
	3	3	yellow, greenish	4-3.7	Uranopilite	$(UO_2)_6(SO_4)(OH)_{10} \cdot 12H_2O$	coatings on pitchbl.,tricl. fibres
	3	3	yellow-green	3.2-3.1	Meta-aut.-Autunite	$Ca(UO_2)_2(PO_4)_2 \cdot 6\text{-}12H_2O$	micaceous, lamellar crystals
	3	3	white-green	2.9-2.8	Andersonite	$Na_2Ca(UO_2)(CO_3)_3 \cdot 6H_2O$	ylw grn; pseudo cubic, rare
	3	3	white-green	2.5	Schroeckingerite	$NaCa_3(UO_2)(CO_3)_3(SO_4) \cdot F \cdot 10H_2O$	flrcence also ylwsh grn; micaceous
	3	3	apple green	2.4	Liebigite	$Ca_2(UO_2)(CO_3)_3 \cdot 10H_2O$	crusts and platy crystals
	3	3	yellow-green	2.3	Swartzite	$CaMg(UO_2)(CO_3)_3 \cdot 12H_2O$	prismatic, rare
			weakly and medium fluorescent			
	-	1	yellowish	3.8-3.5	Sklodowskite	$Mg(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$	minute rhombic prisms, rare
	1	1	bluish green	3.3	Voglite	Ca, Cu, UO_2 - carbonate + H_2O	resembles torbernite, coatings on pitchblende, rare
	?	?	yellow-green ?	3.3	Sharpite	$(UO_2)CO_3 \cdot H_2O$?	fibrous crusts, rare
	?	?	yellowish green ?	2.6	Rabbittite	$Ca_3Mg_3(UO_2)_2(CO_3)_6(OH)_4 \cdot 18H_2O$	pale grn; bundles of minute fibres, rare
Non-fluorescent Min.	-	-		5.4-5.3	Cheralite	$(Ce, La, Th, Ca, U)(P, Si)O_4$	pale, dark green; brittle masses, rare
	-	-		5.3-4.9	Vandenbrandeite	$Cu(UO_2)O_2 \cdot 2H_2O$	dark green, occ.black; tabular, rare
	-	-		4	Sengierite	$Cu(UO_2)(VO_4)(OH) \cdot 4\text{-}5H_2O$	empire grn; rhombic plates, rare
	-	-		3.8-3.6	Meta-zeunerite	$Cu(UO_2)_2(AsO_4)_2 \cdot 6\text{-}8H_2O$	platy, like torbernite
	-	-		3.7-3.5	Metatorbernite	$Cu(UO_2)_2(PO_4)_2 \cdot 6\text{-}8H_2O$	emerald green; micaceous
	-	-		3.6-3.4	Zeunerite	$Cu(UO_2)_2(AsO_4)_2 \cdot 8\text{-}16H_2O$	dark green, not found in nature, rare
	-	-		3.6-3.3	Tyuyamunite	$Ca(UO_2)_2(VO_4)_2 \cdot 5\text{-}8.5H_2O$	yellowish green; micaceous, pulverulent
	-	-		3.6-3.2	Torbernite	$Cu(UO_2)_2(PO_4)_2 \cdot 8\text{-}12H_2O$	emerald green; micaceous
	-	-		3.5	Cuprosklodowskite	$Cu(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$	pale grn-ylw; minute rhombic prisms, rare
	-	-		3.3	Johannite	$Cu(UO_2)_2(SO_4)_2(OH)_2 \cdot 6H_2O$	reniform aggreg., minute prism. crystals

FIG. 4.

	Non-fluorescent	Fluorescent					
RED or ORANGE MINERALS							
	-1	-1	dull brownish, violet	6.4-3.9	"Gummite"	Mixt. of U-min., some flrcent	gum-like
	3	?	orange-red	4.6-3.3	Zircon	$ZrSiO_4$	brownish red; see above
	2	1	pale yellow	4-3.8	Uranophane, U-til	$Ca(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$	occ.orange; fibr.,mass.,rad. aggreg.
	-	-		7.3-7.1	Curite	$3PbO \cdot 8UO_3 \cdot 4H_2O$	occ.orange-red; acicular
	-	-		6.7-5.9	Kasolite	$Pb(UO_2)(SiO_3)(OH)_2$	occ. rdsh brwn; prismatic, rare
	-	-		6.4	Uranospherite	$(Bi0)(UO_2)(OH)_3$?	orange-yellow, brick red; hemispheres, rare
	(-1)	(-1)		6.4-3.9	"Gummite"	Mix. of U-min., some flrcent	gum-like
	-	-		6	Fourmarierite	$PbO \cdot 4UO_3 \cdot 7H_2O$	golden yellow; rhombic, platy crystals
	-	-		5.5-4.6	Monazite	$(Ce, La, Y, Th)PO_4$	occ. orange-yellow; flat prism.
	(3)	?		4.8-3.9	Zircon	$ZrSiO_4$	occ. reddish brown; see above
	-	-		4.6-3.3	Ampangabeite	$(U, Y, Er, Th, Ca)_2(Nb, Ta, Fe, Ti)_7O_{18}$?	occ. reddish; rounded, rad.,prism. aggreg., rare
	-	-		?	Rauvite	$CaO \cdot 2UO_3 \cdot 2V_2O_5 \cdot 16H_2O$?	occ. purple-red; earthy masses, rare
COLORLESS MINERALS							
	1	?	dull white,pink tinge	7.1	Huttonite	$ThSiO_4$	colorless; pale cream, grains in beach sands, rare
	3	?	orange-red	4.8-3.9	Zircon	$ZrSiO_4$	rdsh brwn,ylw,gray,grn;prismatic, pyramidal
	-	-		6.4-6.3	Microlite	$(Na, Ca)_2Ta_2O_6(OH, F)$	pale ylw,brwn,grn; grains, masses, octahedrons
	-	-		5.5-4.6	Monazite	$(Ce, La, Y, Th)PO_4$	brown, pale yellow, flat prisms
	-	-		5.1-4.4	Xenotime	YPO_4	ylwsh or rdsh brwn,gray,ylw,grnsh; zircon habit
	(3)	?		4.8-3.9	Zircon	$ZrSiO_4$	see above

FIG. 5.

so-called secondary uranium minerals it is a prominent and fairly consistent quality. In all cases where a single mineral species is known to occur in more than one color or where the color is such that it cannot be readily identified or described, the mineral is listed within more than one color group.

Colors and intensities of fluorescence are given for both the short-wave (2537 AU) and the long-wave (3660 AU) ultraviolet light.

The remarks at the right side of the tables include the most important color variations, crystal habit, and other easily recognized properties. These data often are helpful in making a specific decision concerning the mineral in question.

Use of the table can be illustrated by means of the following example. A green radioactive mineral fluoresces a strong greenish yellow, a combination of properties that corresponds to a group containing seven possible minerals—three carbonates, two phosphates, one sulfate, and one mixed carbonate-sulfate. Simple chemical tests would indicate which of these is in question. Should the mineral prove to be a sulfate, we then know that it must be uranopilite; should it be a phosphate and contain barium, we then know that it must be meta-uranocircite, and so on. Determination of specific gravity generally restricts an unknown mineral to a small group, but in many cases this test is not necessary for a field determination.

Many of the minerals included in the table are extremely rare, and have been reported from only one or two localities. Thus, once an unknown mineral is assigned to a certain group, the number of possibilities can be greatly reduced by over-looking the very rare minerals, especially for preliminary determinative work.

The table shows that the uranium minerals, when grouped according to color and fluorescence, show some systematic trends in chemical composition that can be used in predicting composition for further testing. Thus the first group of black, dark-brown, or brown thorium- and uranium-bearing minerals includes most of the rare-earth-, niobium-, tantalum-, and titanium-bearing minerals and other complex oxides. These minerals are prevailingly non-fluorescent and heavy, with specific gravities between 10.5 and 4.5 for fresh, unaltered material. Only allanite has a specific gravity of 4.2 and lower. Only some zircon is strongly fluorescent; other minerals of this group might fluoresce, but only because of alteration products on their surfaces.

The two groups of colorless and red or orange minerals have characteristics similar to the above-described group. The occasionally orange uranophane and the colorless huttonite both have a weak but distinct fluorescence. Most of the minerals in these two groups are not consistently of one color, and hence are also included within the other yellow-, green-, or black-colored groups. The yellow and green fluorescent minerals are divided into strongly and weakly fluorescent subgroups to facilitate identification.

The eleven strongly fluorescent yellow minerals are mostly hydrated uranyl phosphates, uranyl carbonates, and uranyl sulfates (plus one uranyl silicate, one uranyl arsenate and one hydrated uranium oxide) of calcium, barium, alkalies, or aluminum. None of these minerals contain heavy-metal cations. Among the weakly fluorescent minerals only one (renardite) is a lead mineral

and one (carnotite) is a vanadate. The fluorescence data on both are questionable, and hence both appear also in the non-fluorescent group. Most other minerals of the weakly fluorescent group are also hydrated uranyl phosphates, silicates, arsenates, and carbonates of magnesium, calcium, and potassium. No essential heavy metals are present.

The non-fluorescent group of yellow uranium minerals includes mainly uranyl vanadates, phosphates, silicates and arsenates of heavy metals, such as lead, bismuth, and iron. One uranyl silicate of copper also occurs in the green-minerals group. The important calcium and potassium minerals of the yellow group, tyuyamunite, meta-tyuyamunite, and carnotite, are all vanadates.

The group of green uranium minerals provides a very clear example of the arrangement of uranium minerals into fluorescent and non-fluorescent groups, depending on their chemical composition. The strongly fluorescent minerals of this group are hydrated uranyl carbonates and phosphates of calcium, sodium, and barium, and one hydrated uranyl sulphate, uranopilite, also is included. In the weakly fluorescent group the composition of the copper-bearing calcium uranyl carbonate, voglite, is not certain. All known copper uranyl phosphates, vanadates, arsenates, one silicate (cuprosklodowskite), and one sulphate (johannite), belong to the non-fluorescent group of green radioactive minerals.

It is evident from the foregoing that the presence of such elements as copper, lead,[1] vanadium, bismuth, and perhaps iron inhibits or prevents the fluorescence of uranium minerals. It can be assumed that the variable intensities of fluorescence in numerous uranium minerals are due to variations in composition, particularly to the presence or absence of these elements. Fluorscence can also result from fluorescent inclusions, as in the case of torbernite, Lyon (15).

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EXPLANATION OF SYMBOLS AND ABBREVIATIONS

AU—Ångström units (1 AU = 10^{-8} cm)
2537—Short-wave ultraviolet light
3660—Long-wave ultraviolet light
I—intensity; − no fluorescence, −1− very weak, 1− weak, 2− medium, 3− strong
Sp.gr.—Specific gravity
(3)—Occasionally fluorescent; intensity shown within brackets

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SUPERGENE COPPER–URANIUM DEPOSITS IN NORTHERN NOVA SCOTIA

J. J. BRUMMER

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ABSTRACT

Very low-grade, uneconomic uranium mineralization occurs over a large area of northern Nova Scotia. It is associated with chalcocitized carbonized plant fragments that occur in gray continental sediments of the Pictou Formation (Upper Pennsylvanian). Typically the plant fragments occur in conglomerates, grits or arkoses that fill stream channels in underlying red mudstones. The copper and uranium mineralization are closely associated, are related to the presence or absence of coaly fragments, and are of supergene origin. The deposits investigated proved uneconomic, but are similar to those of the Colorado Plateau region of the southwestern United States. Some 26 shallow drill holes totalling 3,089 feet have been drilled to investigate the deposits.

INTRODUCTION

Copper mineralization in the Carboniferous "Red Bed" sediments in the provinces of New Brunswick and Nova Scotia has long been known. The

more important of these deposits in New Brunswick are the Dorchester Prospect, Westmorland County; and the New Horton, Midway and Goshen Prospects, Albert County. In Nova Scotia, Fletcher (4, 5, 6) has indicated the presence of about 40 copper occurrences in the Cumberland, Colchester and Pictou Counties. Sporadic attempts to mine some of the above have been made since the end of the last century. In Nova Scotia, numerous old adits and shafts attest to the widespread interest in the occurrences. None of these workings are large and only a few extend for more than a hundred feet down the dip. Most of the mining activity took place at the end of the last century. Records of the early work are meagre and all the openings

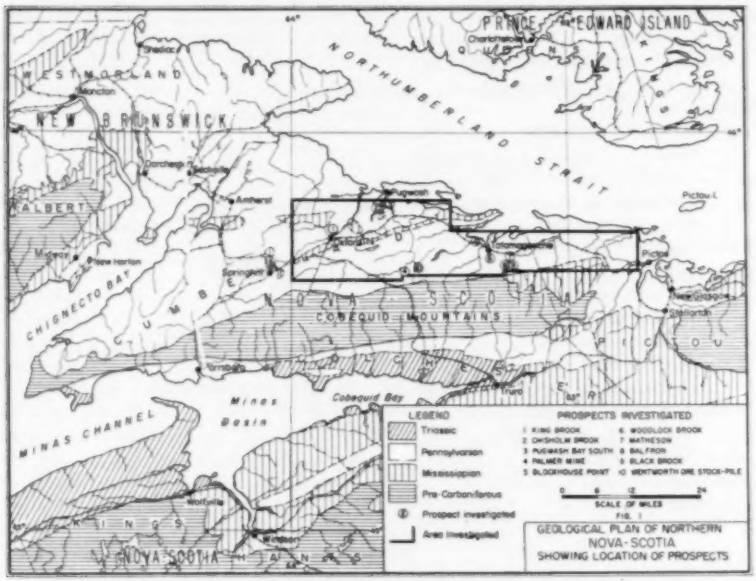


FIG. 1.

are inaccessible. During the past fifty years, several companies have re-examined the old showings but no serious attempts have been made to investigate the down-dip extensions.

The present interest in the area was aroused by the widespread occurrence of copper showings and the suggested existence by Hugh Fletcher of two horizons of copper-bearing beds each having a strike length of over 43 miles. This suggested a possible syngenetic sedimentary copper province.

Acknowledgments.—The observations described in this paper were accumulated during the fall of 1955 while investigating the mineral potential of the Maritime Carboniferous province on behalf of Kennco Explorations

(Canada) Ltd. Permission to publish has been granted by the above company and by Kennecott Copper Corporation of New York. The author is indebted to the following for a critical review of the paper: Mr. C. J. Sullivan, Kennco Explorations; Dr. J. W. Gruner, University of Minnesota, and Dr. H. R. Steacy, Geological Survey of Canada. The writer was guided in this work by the excellent reports available on the area by J. P. Messervey (8), M. F. Bancroft (1), D. A. Barr (2), G. Shumway (10). Finally the writer wishes to record his appreciation of the everready and willing services rendered by his assistant, Mr. Grant Sawyer.

Location.—The occurrences described in this paper are found over an area of 500 square miles that extends from the Northumberland Straight in the north to the Cobequid Mountains in the south, and from Pictou in the east to about seven miles west of Oxford (Fig. 1).

TOPOGRAPHY

The area forms part of the Cumberland-Pictou lowlands located north of the upland formed by the Cobequid Mountains. It consists of a gentle rolling surface of mature relief that rises to elevations averaging little over 250 feet with a few interruptions. These lowlands are underlain by less resistant rocks of Carboniferous age, such as sandstones, shales, limestones and gypsum, which have allowed erosion to proceed at a more rapid rate than the resistant older formations to the south.

The flat relief of the area has resulted in a scarcity of outcrops; bedrock is exposed only along the shore and along the northward-flowing rivers and streams.

GENERAL GEOLOGY

The area forms part of the Cumberland Basin of deposition, the greater portion of which is underlain by two shallow synclines of upper Pennsylvanian Pictou Series. These are separated by the Clairmont anticline that strikes northeast to southwest across the western half of the area and along which rocks of the underlying Claremont, Middleborough and Windsor Series are exposed. The southern limit of the basin is formed by the Pre-carboniferous Cobequid Mountains. The sequence of formations [1] is shown in Table I.

The area studied and the prospects investigated are all located in synclines of Pictou Formation that cover the major portion of the area.

Pictou Formation

The Pictou Formation is characterized by its predominantly red-colored sediments. It consists of micaceous, dark-red to purple-red shales and mudstones with interbedded sandstones. The sandstones are red and gray in color, generally coarse-grained and arkosic, the felspar being pink in color. Clay pebbles are common, forming clay-pebble conglomerates arranged as lenses or scattered irregularly throughout a sandstone bed. Cross-bedding, ripple marks, and stream channelling are common throughout.

TABLE I

Period	Epoch	Group/Formation	Description
Carboniferous	Pennsylvanian	Pictou (7,000 ft. thick)	Red arkosic sandstone, shale, mudstone, grit and conglomerate. Some gray arkosic sandstone and shale which are occasionally radioactive and copper bearing. (Continental deposit)
		Cumberland (7,000 ft. thick)	Gray and red sandstone, grit and conglomerate: red shale.
		Boss Point	Gray to red, interbedded sandstone and shale.
		Claremont	Red conglomerate and grit, some sandstone and shale.
	Mississippian	Windsor	Red shale, gypsum, limestone, gray shale and calcareous shale. (Marine)
Pre-carboniferous			Sedimentary and volcanic rocks, intruded by granite, diorite, etc.

[1] After Norman & Bell (1938 and 1945) with minor additions by the author.

ECONOMIC GEOLOGY

Occurrence of Sulfides

Sulfides occur only in the light-gray sandstone, arkose, and shale layers, which are thin, lenticular, and occur interbedded with red mudstones [2] or red-brown argillaceous sandstones at four or five different horizons in the sequence. The minerals are erratically distributed throughout the gray sediments and are invariably associated with carbonized plant fragments. Pyrite is the chief sulfide present with lesser amounts of chalcocite and covellite, and rare traces of chalcopyrite and bornite. Sulfides occur as:

a) Nodules or concretions, 1–2 inches in diameter, of pyrite or pyrite partly replaced by chalcocite with traces of covellite. The concretions are mostly restricted to a particular bed along which they occur at irregular intervals (Fig. 6).

b) Replacing carbonaceous layers, several millimeters in thickness, along bedding in shales and sandstones. Sandstones are commonly cross-bedded (Fig. 2).

c) Disseminated specks and clusters of sulfides in sandstones and shales, generally associated with minute specks of carbonaceous material (Fig. 5).

d) Replacing fragments of coaly material that occurs in conglomerate or gritty lenses, commonly at the base of light gray arkoses that fill stream channels in red mudstones. Where carbonized plant remains are replaced,

[2] The term "mudstone" used in this investigation applies to a soft, dark red-brown, sediment that commonly disintegrates on exposure to air. Its most conspicuous feature is absence of bedding.

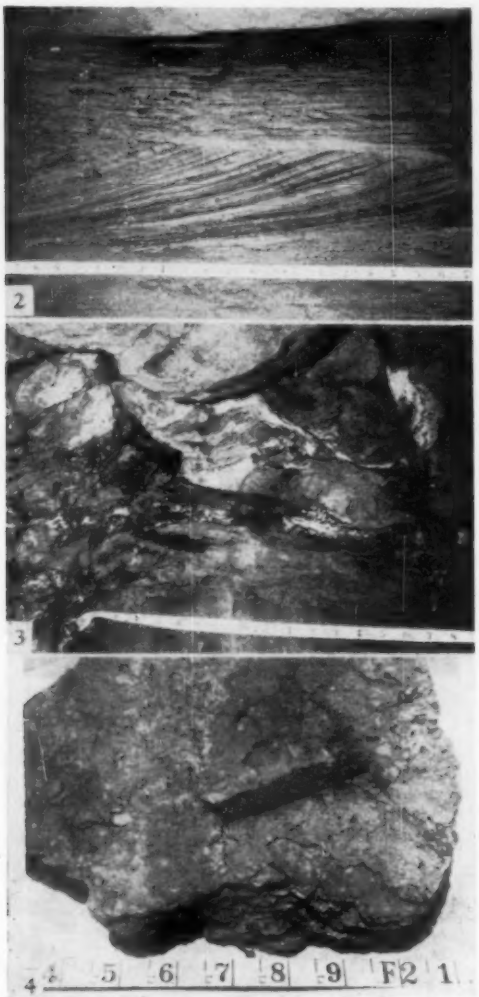


FIG. 2. Cross-bedded gray sandstone with thin carbonaceous separations along fore- and bottom-sets that are stained green by malachite. Exposed along sea cliff at Blockhouse Point Prospect.

FIG. 3. Radioactive cupriferous coal fragment in conglomeratic grit. Sulfides present are pyrite, chalcocite and covellite. Exposed along sea cliff at Blockhouse Point Prospect. Log assays: 17.65% Copper, 17.42% Carbon, 0.051% U_3O_8 (equivalent).

FIG. 4. Radioactive coaly plant fragment in shale-pebble conglomerate. Stained green by malachite. From Wentworth stockpile.

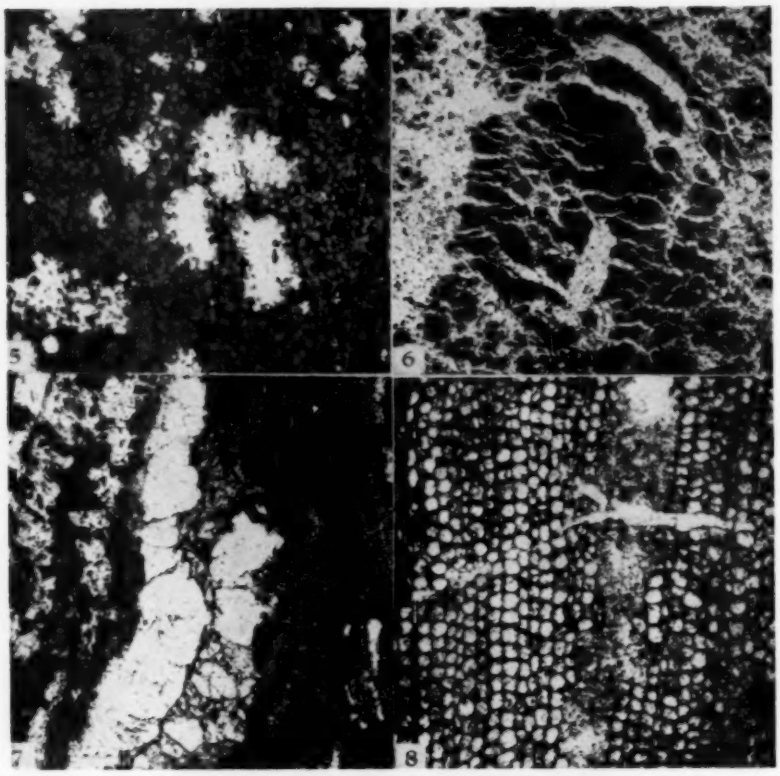


FIG. 5. Clusters of pyrite grains in light-gray carbonaceous sandstone. From Pugwash Bay South Prospect. × 11.

FIG. 6. Chalcocite (white) replacing pyrite (dark) in coaly nodule from Chisholm Brook Prospect. × 11.

FIG. 7. Fragment of coal showing different stages of replacement by pyrite. Note cell replacement on right and left center and massive replacement in center. From King Copper Prospect, D.H. No. 4 at 113.7 ft. depth. × 11.

FIG. 8. Rounded plant cells in coal replaced by pyrite. Note veinlet of chalcocite cutting across pyrite. Location same as Fig. 7. × 56.

the enclosing sandstone or arkose is generally mineralized for an inch or two around the fragment by specks of interstitial sulfides. Fragments of sulfide-bearing coaly material range in size from ¼ inch to 2 feet in length but average 1 to 4 inches in size. Distribution of coaly fragments is erratic and discontinuous (Figs. 3, 4).

Pyrite is the most abundant sulfide present and occurs as concretions in sandstones with or without a nucleus of coaly material as listed under (a). The concretions show concentric layering of different grain size pyrite.

Where associated with carbonaceous material occurring as listed under (b), (c) and (d) above all stages of the replacement of the woody structure can be noted ranging from wood-cell replacement to complete replacement (Figs. 7, 8). Where it occurs disseminated in sandstone as in (c) it appears to be associated with thin slivers of carbonaceous material that also occurs in the sandstone.

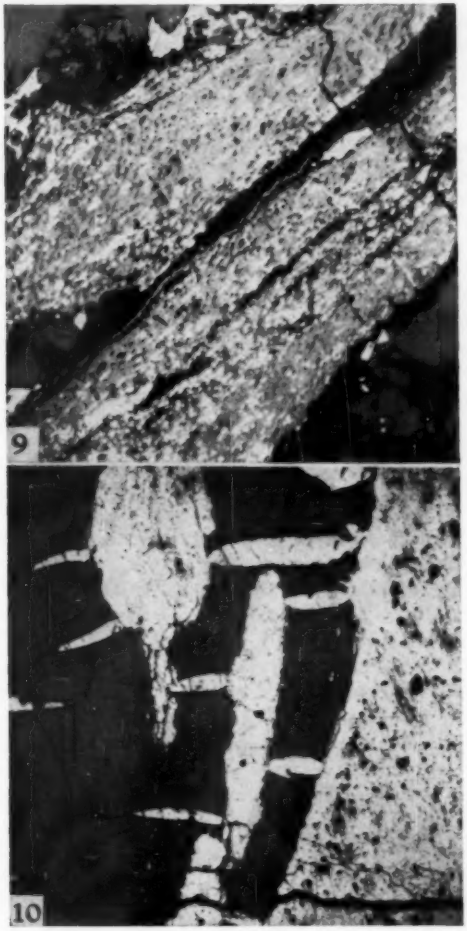


FIG. 9. Coal fragment in sandstone replaced directly by chalcocite (white). From Dorchester Mine, N. Brunswick, DH V2. at 47 ft. depth. × 56.

FIG. 10. Chalcocite (white) replacing coal (dark gray) and also filling cracks. From Black Brook Prospect. × 11.

Chalcocite and covellite generally occur together with the former predominating and the latter present in trace amounts. Chalcocite commonly occurs as nodular masses replacing pyrite (Fig. 6), which in turn is associated with coaly nodules as in (a), (b), or (d) listed above. However, pyrite is not always present and chalcocite occurs alone replacing and filling fractures in coaly material (Figs. 9, 10). It also occurs disseminated in sandstone that contains microscopic fragments of carbonaceous material. Covellite occurs in minor amounts replacing the chalcocite and in places pyrite directly without the presence of chalcocite. Both of these sulfides occur in minor amounts when compared with the widespread distribution of pyrite. Oxidation of chalcocite has resulted in the green malachite-stained sandstones that attracted attention of the early investigators.

Chalcopyrite and Bornite.—Rare specks of these two sulfides have been noted in one locality, Woodlock Brook, where they occur disseminated with pyrite and chalcocite in a sandstone. The bornite and chalcopyrite are replaced by covellite.

Paragenetic Relations

From the above descriptions it will be seen that pyrite was the first sulfide to be deposited. That it replaces the plant cells of the woody material indicates the replacement took place before carbonization of the material. Pyrite was later replaced by chalcocite and covellite. Some of the chalcocite replaced the coaly material directly without the presence of earlier pyrite. The minor amounts of chalcopyrite and bornite are considered to be of the same age as the pyrite—all of which are replaced by covellite and chalcocite.

INVESTIGATION OF THE PROSPECTS

Nine of the numerous copper occurrences found in the area were investigated in some detail by diamond drilling (Fig. 1). These prospects are: 1. Matheson, 2, Woodlock Brook, 3. Balfron, 4. Black Brook, 5. Blockhouse Point, 6. Palmer Mine, 7. Chisholm Brook, 8. Pugwash Bay South, 9. King Brook.

At most of the prospects, the surface mineralization consists of malachite-stained sandstones and conglomerates. Assays of selected specimens from surface exposures ranged up to 67.76% Cu but at distances of 50 feet or more down the dip of the beds the copper content had decreased to less than 0.1% Cu. The conglomeratic layers are lenticular, and fill erosion channels in the underlying red mudstone. The thickness of the conglomerate layers averages about 6 inches and rarely reaches 12 inches.

Some 21 shallow drill holes, totalling 2425 feet, were drilled by Kennco Explorations (Canada) Ltd. and 5 holes, totalling 664 feet, by King Copper Mining Corp., to investigate the down dip extensions of the mineralized beds. In all cases the mineralization changed, down the dip, from chalcocite and pyrite to pyrite with mere traces of chalcopyrite; the primary minerals also, are associated with carbonaceous material.

The drilling has indicated conclusively that the chalcocite and associated minor covellite mineralization is a surface feature that does not extend down

the dip of the beds for more than a few tens of feet. Its restriction to the present day water table, its constant association with covellite and its occurrence replacing pyrite all indicate that it is of supergene origin.

RADIOACTIVITY

The discovery that the cupriferous carbonized plant fragments were also radioactive led to the investigation of the occurrences for their radioactive content. One of the best sources of radioactive material is the Wentworth ore stockpile.

Wentworth Ore Stockpile

On the farm of Mr. Tratt at Wentworth Center is an old ore stockpile on the plant site of the former Cumberland Copper Company. This company was formed to treat ore from the small deposits in the area, presumably on a customs basis. Several tens of tons of ore are present on the site. The ore consists of fragments of light gray sandstone and conglomerate stained green by malachite. The malachite formed is the result of weathering of chalcocite associated with films of carbonized plants along the bedding of sandstone fragments, or as carbonized logs and fragments occurring in shale-

TABLE II

ASSAYS OF SELECTED SPECIMENS FROM SOME OF THE PROSPECTS

Sample No.	% Cu	% C	% U_3O_8 (equiv.)	
639	12.59	4.38	0.030	Hand-cobbed to give large proportion of carbonaceous material
640	13.88	5.18	0.035	
641	8.74	2.03	0.028	Sandstone fragments rich in plant remains
642	9.16	1.13	0.026	
643	6.26	1.43	0.016	
644	5.67	2.04	0.024	
645	5.30	0.40	0.024	
646	6.49	1.89	0.023	
658	17.65	17.42	0.051	Chalcocitized coaly material from conglomerate
659	1.61	17.42	0.051	Specially hand-cobbed to include larger amount of carbonaceous separations than normally present
660	1.44	8.56	0.042	
661	0.80	6.20	0.039	Laminated light-gray sandstone with carbonaceous separations along bedding
662	0.94	9.14	0.038	
663	0.49	60.85	0.015	Selected specimens of chalcocitized coaly material from conglomerate
651	67.76	3.04	0.047	
652	65.34	5.45	0.071	
655	60.13	2.52	0.025	

Location of samples: Nos. 639–646 Wentworth Ore Stockpile
658 Blockhouse Point
659–662 Woodlock Brook
663 French River (at Tatamagouche)
651–652 Black Brook
655 Chisholm Brook

pebble conglomerates. Minor amounts of chalcocite replace pyrite nodules in sandstone.

The fossil plants have been identified as varieties of *calamites, cordaites, sigillaria* or *lepidodendron* (7) (Fig. 4).

Table II gives the assays of selected samples (Nos. 639–646) from the stockpile.

These results show the samples to contain high amounts of copper but low uranium values. The material, however, represents specially selected samples from an ore stockpile and must not be regarded as typical of the

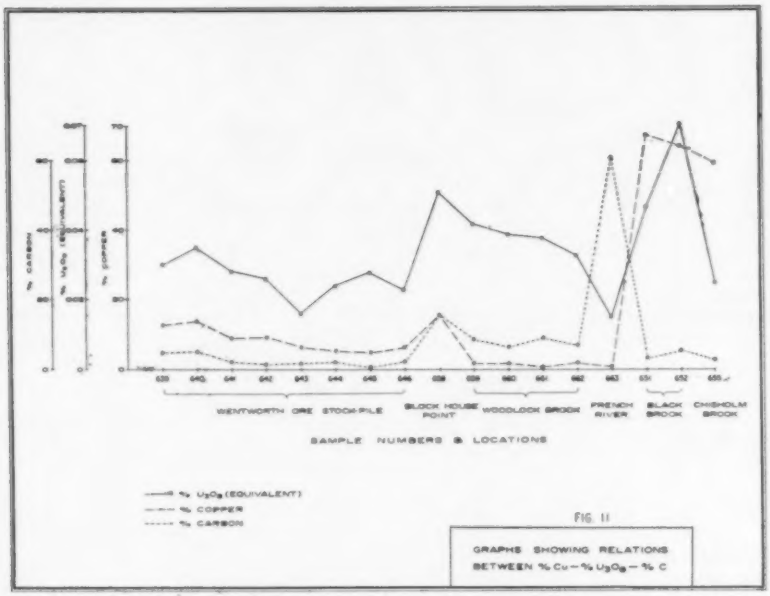


FIG. 11.

mineralization in place at the prospect. The mineralized widths are up to a few inches only.

Scintillometer readings over the dumps ranged from 0.0385 to 0.056 MR/HR which is four to six times the background reading of 0.010 MR/HR.

Relation of Copper-Uranium-Carbon Content

The results of the samples from the different prospects investigated are listed in Table I, and have also been plotted as graphs to show the relationship between copper-carbon-uranium content (Fig. 11). In general, it will be noted that there is a sympathetic relation between the three components. These samples all represent specially selected specimens and the highest

radioactive content recorded was 0.071% U_3O_8 (equivalent) from the Black Brook Prospect. The average content ranges between 0.02 to 0.04% U_3O_8 (equivalent). These amounts do not represent ore grade even if the tonnage was present.

The radioactive mineralization is associated with the coaly material and occurs only where supergene chalcocite is present. Pyritic coaly material, pyrite nodules, or coaly material alone, are non-radioactive or only very slightly radioactive. Since the radioactivity, like the copper mineralization, is restricted to the upper sections of the beds, it also is considered to be of supergene origin.

The following are extracts from a report by the Radioactivity Laboratory, Mineral Deposits Division, Geological Survey of Canada, on samples of radioactive, chalcocitized, coaly material, from the Black Brook prospect, submitted by the writer for identification purposes:

> The radioactivity . . . is found to be associated mainly with a black, carbonaceous, coal-like material. A hand-picked sample of this material showed a radioactivity of 0.39% U_3O_8 equivalent, whereas a portion of pulverized sample washed free, or apparently so, of the carbonaceous matter showed only 0.02% U_3O_8 equivalent. An ash determination on the hand-picked material yielded a value of 11.9%. This value is evidentally high, however, because some foreign matter was observed in the ash. A diagnostic analysis showed that the radioactivity of the ash was due to uranium, but we would not be able to say in what form the uranium is present. Recent studies of these carbonaceous materials have shown that in some materials the uranium is most likely present in the ionic state, and that in other materials, it occurs as discrete grains of radioactive minerals, which can be identified only by exhaustive study. We were not able to identify any radioactive minerals in the material from your sample by ordinary laboratory methods. (11)

Special radiometric tests on samples indicate that the material is out of equilibrium as is indicated by the following results:

Beta activity:	0.071% U_3O_8 equivalent.
Gamma activity:	0.040% U_3O_8 equivalent.

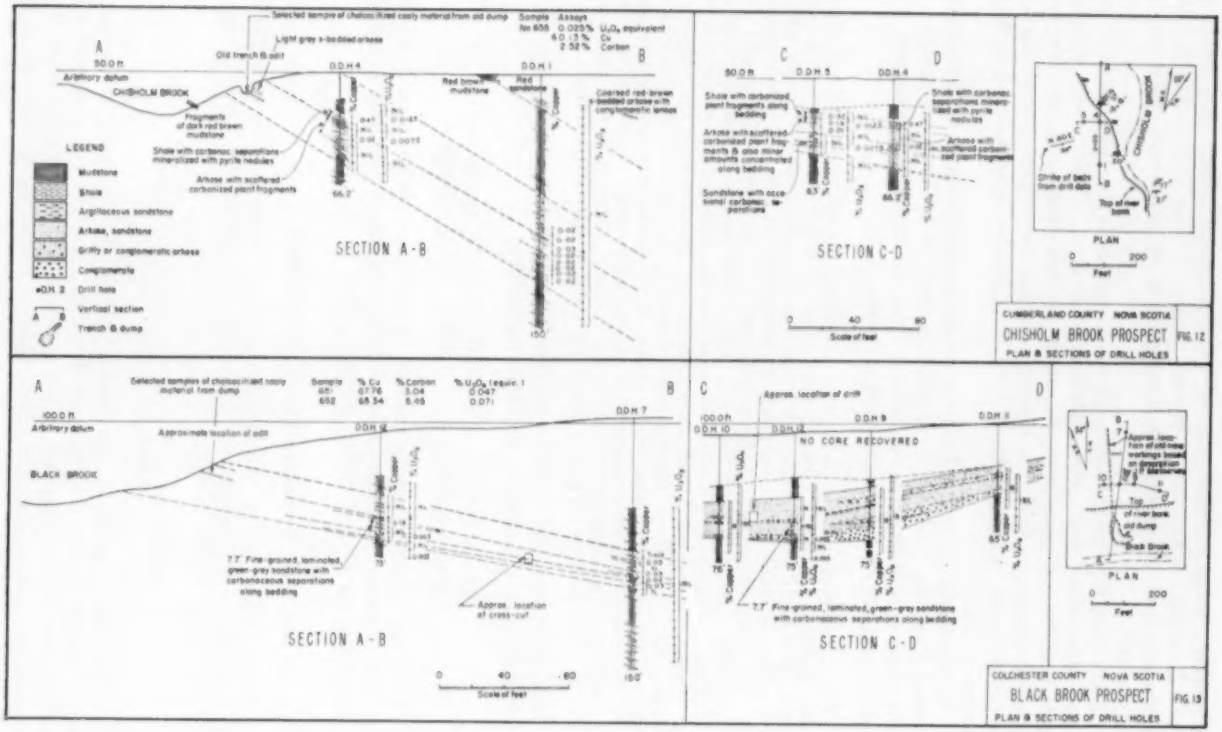
Since the copper is mainly present as supergene chalcocite and covellite, it is safe to assume that the radioactive material has been brought in by the same agency, namely, circulating ground waters.

DESCRIPTION OF PROSPECTS

A brief description of two prospects is given below as being typical of the many occurrences investigated. These are: (a) Chisholm Brook Prospect, and (b) Black Brook Prospect.

Chisholm Brook Prospect

(Also known as W. A. McPherson's Mine) Chisholm Brook is a small stream that flows into the Pugwash River at a point located about 2½ miles south of the town of Pugwash. The prospect is located on both sides of the brook about ¼ mile upstream (Figs. 1, 12). According to Ells: "Four trial


Selected sample of chalcocitized coaly material from old dump
Sample No 656 Assays 0.025% U_3O_8 equivalent 6.0 :5% Cu 2.52% Carbon
Light grey x-bedded arkose
Old trench & adit
DDH 4
DDH 1
Red brown mudstone
Red sandstone
Coarse red-brown x-bedded arkose with conglomeratic areas
Arbitrary datum
CHISHOLM BROOK
Fragments of dark red brown mudstone
Shale with carbonac separations mineralized with pyrite nodules
Arkose with scattered carbonized plant fragments
66.2'
150'
LEGEND
Mudstone
Shale
Argillaceous sandstone
Arkose, sandstone
Gritty or conglomeratic arkose
Conglomerate
DDH 2 Drill hole
Vertical section
Trench & dump
SECTION A-B
C
D
DDH 5
DDH 6
Shale with carbonized plant fragments along bedding
Arkose with scattered carbonized plant fragments & also minor amounts concentrated along bedding
Sandstone with occasional carbonac laminations
Shale with carbonac separations mineralized with pyrite nodules
Arkose with mineralized carbonized plant fragments
63' % Copper
66.2' % Copper
SECTION C-D
0 40 80
Scale of feet
PLAN
0 200
Feet
CUMBERLAND COUNTY NOVA SCOTIA
CHISHOLM BROOK PROSPECT FIG. 12
PLAN & SECTIONS OF DRILL HOLES
Selected samples of chalcocitized coaly material from dump
Sample No. 652 % Cu 67.78 % Carbon 5.04 6.45 % U_3O_8 equiv. 1 0.047 0.071
1000 ft
Arbitrary datum
Approximate location of adit
DDH 8
DDH 7
BLACK BROOK
7.7' Fine-grained, laminated, green-grey sandstone with carbonaceous separations along bedding
Approx. location of cross-cut
SECTION A-B
0 40 80
Scale of feet
Approx. location of drift
DDH 10
DDH 12
DDH 9
DDH 11
NO CORE RECOVERED
78' % Copper
73' % Copper
65' % Copper
7.7' Fine-grained, laminated, green-grey sandstone with carbonaceous separations along bedding
SECTION C-D
Approx location of old mine workings based on prospection data
Top of river bank
old dump
Black Brook
PLAN
0 200
Feet
COLCHESTER COUNTY NOVA SCOTIA
BLACK BROOK PROSPECT FIG. 13
PLAN & SECTIONS OF DRILL HOLES

pits and a tunnel are on the property. . . . Four or five tons of chalcocite were shipped to Boston, and some tons are now on the site." (3, p. 13)

All of the above mentioned workings have caved-in and are inaccessible. At the entrance of the tunnel is an old dump of weathered, light-gray arkose containing fragments of bright, black coal several inches in size. These coaly fragments have been partly replaced by chalcocite which, in turn, has a coating of malachite. Examination of the chalcocite fragments shows them to contain unreplaced remnants of pyrite. Some of the malachite has impregnated the adjacent sandstone staining it light green. No mineralized beds were found in place.

On the east side of the adit entrance a light gray arkose crops out; it has a strike of S52°W and dips 31° southeast. The gray arkose horizon is overlain and underlain by soft, dark-red-brown mudstones. For the assay results of a selected sample (No. 655) of chalcocitized coaly material from the dump see Table I.

Three holes Nos. 1, 4 and 5 were drilled to investigate the down-dip extensions of the surface exposures. No. 1 was located 180 feet on a bearing of S36°E, from the arkose outcrop and drilled to a depth of 150 feet. The 25-foot thick section of gray arkoses, sandstones, minor siltstones and mudstones gave assay results ranging from 0.02 to 0.03% Cu.

Drill holes Nos. 4 and 5 were located 50 feet apart along the strike of the beds and 55 feet from the arkose outcrop. The arkose bed was intersected in both holes (between depths of 24–45 ft.) carrying scattered carbonized plant fragments. The best assay was 0.02% Cu. The arkose was overlain by a 4-foot shale bed that contains scattered cupriferous pyrite nodules, which gave assays of 0.32 to 0.47% Cu.

The best radiometric assays obtained were 0.0125% and 0.0075% U_3O_8 (equivalent) for samples from the shale and arkose beds intersected in drill hole 5.

Discussion of Results.—These three holes have indicated that no appreciable amounts of copper sulfides or radioactive material extend down the dip of the beds. The radioactive chalcocitized coaly material found on the dump has not been intersected even at shallow depths. The best radioactive results recorded were in D.H. 5. This hole intersected the shale-arkose horizon at a slightly shallower depth (18 to 45 ft.) as compared with D.H. 4 (25 to 53 ft.). This would seem to support the theory that the copper and radioactive material is concentrated close to the surface; i.e. above a vertical depth of 18 to 45 feet or not more than 60 feet down the dip of the beds.

Black Brook Prospect

The Black Brook flows into the Waugh River about 3½ miles southeast of Tatamagouche. The prospect is located 1½ miles upstream from the junction of the north side of the brook (Figs. 1, 13).

The mineral occurrence was worked during 1907 and 1908 by the Sterling Mining Company with production as follows: "1907—650 tons of ore of which 160 tons were shipped, the remainder being left on the dump. 1908—240

tons of ore were shipped to the United States which yielded 28,800 lbs. of copper." (Average grade 5.35% Cu.) (8, pp. 33, 34)

The adit entrance is covered with excavated material and there is not much to be seen except a large pile of shale-peeble conglomerate and light gray sandstone. On the dump, a few pieces of coaly material, partly chalcocitized, can be seen. Some of the sandstone contains disseminated specks of chalcocite and malachite stains. There are no outcrops in the immediate vicinity of the adit.

The chalcocitized coaly material was found to be radioactive and selected hand specimens gave the following assay results (Table I). The content of 0.071% U_3O_8 (equivalent) is the highest value recorded by the author for samples from this metallogenic province.

Five holes, Nos. 7, 9, 10, 11 and 12, were drilled to investigate this prospect. Holes 9, 10, 11 and 12 were spaced 50 to 80 feet apart along the strike of the beds to intersect the conglomerate horizon at 37 to 64 feet depth below the surface or 115 feet downdip from the outcrop. The results indicate that the gray sediments fill an erosion channel in the underlying mudstone and that the individual beds are lenticular with short strike lengths. The coaly fragments represent vegetation entrapped in the sediments during deposition. Their distribution is sparse and erratic. The only carbonaceous material intersected in these few holes was a 7.7-foot bed of laminated sandstone with thin carbonaceous separations along the bedding. A 5.0-foot sample from this bed gave a copper assay of 0.18% Cu, which is the best recorded from the holes drilled on this prospect. All of the holes, except for two samples from D.H. 12, returned results of zero percent U_3O_8 (equivalent). These two samples gave values of 0.005% U_3O_8 (equivalent).

Discussion of Results.—A study of the dump material shows mineralization to exist in the form of chalcocitized radioactive coaly material and disseminated specks of chalcocite in sandstone. Previous records indicate that a fair amount of the ore must have been present to allow shipments of 240 tons. Diamond drilling has indicated that the beds are very lenticular, have short strike lengths and fill old erosion channels. Insufficient down-dip drilling was done to define the direction of these channels. The mineralized coaly material occurs as fragments in the sediments and has an erratic distribution. None of the holes intersected any mineralization. This would indicate that if the mineralization extended down the dip of the beds it must be very localized to have been missed by the four closely-spaced holes.

ORIGIN OF THE DEPOSITS

Diamond drilling has shown that the copper and radioactive mineralization does not extend to below the present water table (25–60 feet below surface as measured in wells). The down dip extensions are slightly cupriferous, non-radioactive pyrite. The writer considers that the chalcocite was formed as the result of weathering and subsequent enrichment of the primary, slightly cupriferous, pyrite. The uranium must have been concentrated by a similar process, even though it is not possible to point to the original source of the

material other than the sediments in which it now occurs. The writer considers that the cupriferous pyrite was deposited with the sediments either contemporaneously or shortly after deposition—but before lithification and destruction of the plant cells by coalification. This deposition took place under reducing conditions (?) in which the light gray sediments were deposited, and not under the oxidizing conditions under which the red mudstones and argillaceous sandstones were laid down. The source of the heavy metals could conceivably have been the nearby Pre-carboniferous Cobequid Mountains.

The restriction of the supergene enriched zone of copper and uranium to a distance of 20 to 50 feet down the dip of the beds coincides with the present position of the water table (25 to 60 feet). Since the gamma activity of the samples is low it might be interpreted that the uranium is of recent deposition and has not yet reached equilibrium. Those features would suggest that enrichment took place during Pleistocene to Recent times.

These deposits are very similar to those occurring in the late Paleozoic, Mesozoic and early Tertiary sediments of the Colorado Plateau region. The author feels that the theory for concentration by multiple migration-accretion as advocated by J. W. Gruner (12) for the Colorado Plateau deposits may well be applied to these Nova Scotia deposits.

The writer would like to draw attention to a similar occurrence of sulfides at Cape George, Nova Scotia recently described by R. G. Wiese, Jr. (13).

ECONOMIC POTENTIAL

The low grade of the deposits (best result recorded 0.071% U_3O_8 (equivalent), the narrow widths, which are measured in inches, the lenticular nature of the beds, and finally the limited extension down the dip of the beds (20–50 ft.) indicate that the deposits investigated do not have any economic potential at present prices.

NORTHWESTERN EXPLORATIONS LTD.,
SUITE 1111, 1030 WEST GEORGIA ST.,
VANCOUVER, B. C.,
Oct. 16, 1957

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DESIGN OF SIMPLE PUNCHED CARD SYSTEMS WITH REFERENCE TO GEOCHEMICAL PROBLEMS[1]

IRVING A. BREGER

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ABSTRACT

A number of critical factors should be considered in the design of files using marginally punched cards. These factors are discussed in general terms and exemplified by reference to a system developed for use in geochemical studies.

INTRODUCTION

THE use of punched cards has been looked upon as a panacea by many faced with difficult bibliographic or classification problems; it usually takes but moderate consideration, however, to realize that punched cards serve only as an aid and are not in themselves a solution. Employment of this codification technique does, moreover, entail many difficulties which frequently show up only after the die is cast and a system has been placed in operation. In these circumstances it is difficult to make corrections, and the final product is only partially satisfactory. It is hoped that the ensuing discussion and expositions will aid the novice in choosing the card and codification system best suited to his requirements.

The variety of coding systems and cards developed during recent years is advantageous in offering numerous choices to the individual setting up a file (1, 2). On the other hand, proper choice of a system has now become, more than ever before, an art rather than a science.

The discussion in this paper is directed to the reader who wishes to set up a small to medium-size catalogue, that is, one containing 1,000 to 20,000 cards. In this range, information can generally be coded satisfactorily on edge-punched cards; entries in excess of 20,000 can probably be made best on cards of the IBM variety. Edge-punched files containing up to 150,000 cards are known, but in such instances it is usually possible to handle subfiles and is, therefore, unnecessary to search the entire file at any one time.

[1] Publication authorized by the Director, U. S. Geological Survey.

The ready accessibility of information entered on edge-punched cards makes it a simple matter to remove duplications, correct errors, and eliminate obsolete information. In this respect, a file such as the one under discussion is equally attractive to an individual recording bibliographic information and to a small business using it to record customer contacts or production or inventory data.

A great advantage of edge-punched cards is the simplicity with which they can be manipulated. Although machines have been developed for the mechanical isolation of desired information (1), it is generally true that hand sorting can be rapidly and accurately effected, even by individuals with but a few minutes of instruction. The simplicity of entering and extracting information from edge-punched card files makes them extremely attractive for those with modest requirements or limited resources.

CHOICE OF CARD

Edge-punched cards are available in numerous rectangular sizes; choice of size is generally governed by the desired perimeter which, in turn, controls the number of items that can be coded on the card. Attempts to increase the perimeter by choosing larger cards are not wholly successful owing to the increased difficulty in manipulating the cards as they get larger. Moreover, larger cards must, of necessity, be made from heavier paper, thus increasing the bulk and cost of a file.

To maintain flexibility in manipulation and strength without bulk, to say nothing of the added cost of large cards, it is wise to choose the smallest card that will satisfactorily serve the specific coding requirements under consideration.

Most cards have four holes to the inch, but it is also possible to obtain cards with five holes to the inch. In so doing, the number of entries on a card is increased by twenty percent, and the choice of a bulky card may be obviated. Also, it is possible to balance card size with coding techniques described below, thereby arriving at a compromise solution in which a small card can be effectively used.

CODIFICATION

There are a number of methods by which a subject can be designated on a punched card.

(1) *Direct coding.*—A particular punch designates a particular subject.
(2) *Numerical coding.*—A subject is designated by a number.
(3) *Alphabetical coding.*—A subject is designated by a letter.

It is possible to use any one of these techniques alone or in combination in any file. Choice of code is, however, related to the number of items to be entered in a system and their degree of interdependence or mutual exclusiveness. This point will be discussed in more detail.

Closely related to the type of code chosen for the entry of information is the technique by which the entry is made. Although small files with a limited

number of entries can use direct coding in which a single punch represents a single subject, most files are more intensive in scope and require additional techniques for the entry of information. One such method commonly used depends upon a "field" of four holes numbered as shown under "year" on the upper edge of Figure 1. It is readily seen that by punching combinations of the holes marked 1, 2, 4, and 7, it is possible to reach the number 14. Thus, four holes make it possible to code numerically and enter fourteen items in this field. By using two fields, the right one for "units" and the left one for

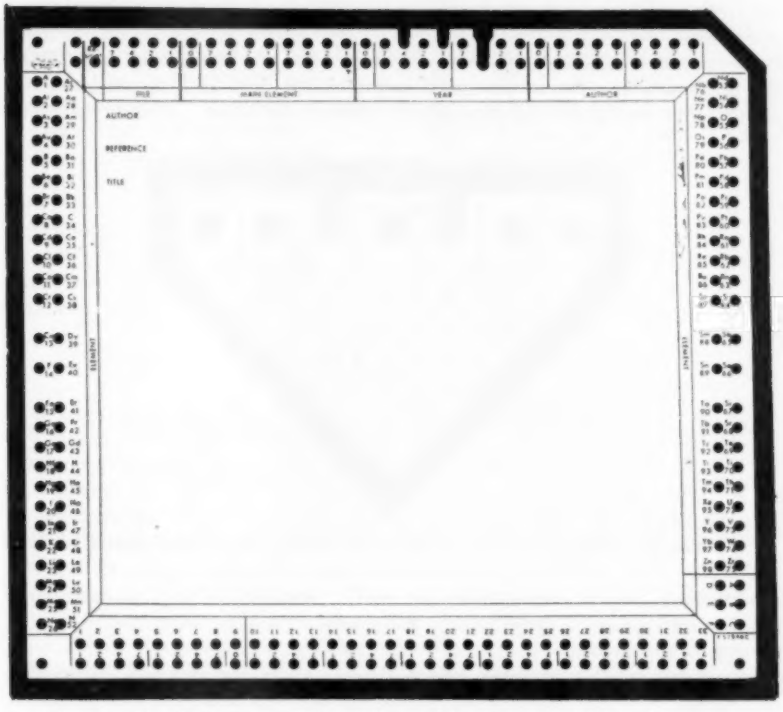


FIG. 1. Punched card used for bibliographic work described in this paper.

"tens," and by limiting the use of each field to nine entries, it is possible to attain 99 entries in two fields with a total of only eight holes. The additional hole, marked "zero," is punched when 10, 20, 30, etc., are indicated and also when 01, 02, 03, etc., are desired. This simple additional punch greatly simplifies the sorting and selection of desired cards.

The double row of holes is also an aid to the selection of cards; deep punches indicate simple numbers in a field, and shallow punches indicate combinations of numbers in the field (3). This is illustrated in Figure 1 where

the year punched is 1954 (the "19" is neglected inasmuch as most entries for this particular file are in the twentieth century). The left-hand field represents a combination of four and one, a compound number, and both punches are shallow; the right-hand field is a simple, deep punch representing the unit, four. Together, both fields indicate that the article coded appeared in 1954. For an article that appeared in 1904, the right-hand field would be punched deep for the digit "four" and the hole marked "zero" would also be punched. In selection, compound numbers in a field can be sorted with shallow-set needles, and simple numbers with deep-set needles. If the appropriate number of needles is used, it is possible to choose cards of the desired year with a single operation.

Application of this simple fool-proof technique can be made in many ways. To code an author, it is necessary only that the first and second letters of names be broken down alphabetically into 99 sub-divisions. Such breakdowns

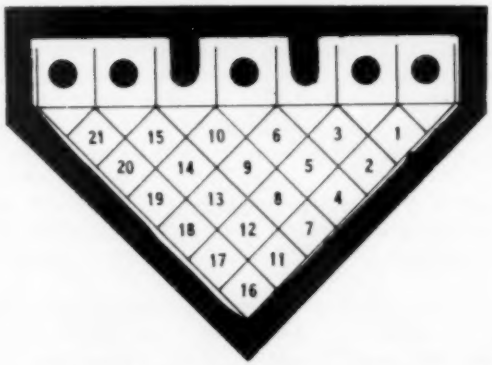


FIG. 2. Triangular code. Punches show the code number "nine."

are available from the card manufacturers. Similarly, it is possible to code 99 chemical elements by punching the number corresponding to the atomic number of the element.

Combination of more than two fields will allow the entry of 999, 9,999, etc., items.

Although this method of entering information is extremely effective and space-saving, there are certain disadvantages to the technique. First, in contrast to simple direct coding where a single punch represents a single subject, it is usually necessary to carry out more than one sorting operation to select the desired cards. The number of operations can be minimized by the simultaneous use of more than one needle, but this in itself is an additional complication not encountered in direct coding. The numerical code, moreover, can be employed only when a single entry is punched in a single field. For this reason, it is possible in the field reserved for "author" in Figure 1 to code only one name even when there are two or more co-authors for a paper.

Numerical codes with triangular fields (Fig. 2) have also been devised and extensively used.

The two punches shown in Figure 2 designate the number "nine," which in turn has been assigned to a specific subject. Combination of any two punches in the seven-hole field can be used to indicate any one of twenty-one numbers.

It is interesting that, although this procedure for entering data is frequently employed, it, too, has a number of disadvantages. Any coding technique is basically designed to enter a maximum number of items in a minimum of space. It is, therefore, interesting to note in Table 1 the number of holes necessary to provide a number of entries. This progression, represented by $\frac{n}{2}(n-1)$ where n is the number of holes in a field, indicates there to be no advantage gained in a five-hole field over direct coding where both shallow and deep punches are used. Although it is possible to code 28 subjects in an eight-hole triangle field, it is important to note that if 1, 2, 4, 7-numerical coding is used without zeros, eight holes in that system will permit the entry of 99 items.

TABLE 1

NUMBER OF ENTRIES IN SINGLE-ROW TRIANGULAR CODING

No. of holes in field	No. of entries
2	1
3	3
4	6
5	10
6	15
7	21
8	28
9	36
n	$\frac{n}{2}(n-1)$

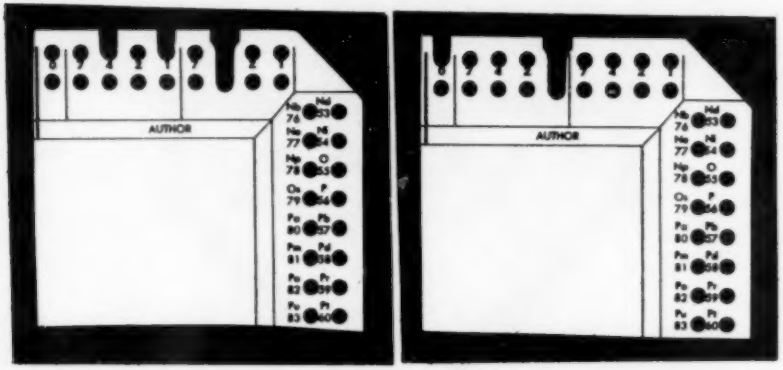
Besides the single triangular coding just described, there is an additional system in which, using a double row of holes, the inner holes represent a triangular diagram in which the items are modified by the outer holes, which also represent a triangular diagram. Thus, the number of entries is represented by $n(n-1)$ where n is the number of holes in an outer or inner field. For a field of six outer and six inner holes, therefore, it is possible to code 30 entries. Obviously, this double triangular system with twice the number of entries is advantageous compared to the single triangular system.

Other variations in the notation of entries are possible and have been described (1). For simplicity in organizing a card file of medium size, however, direct or numerical codes of the type described are suggested.

DESIGN OF FILE

Design of a file system is dependent upon the demands of the user; there are no fixed rules and, consequently, an infinite variety of designs is possible. The organization of a system is best illustrated in the form of the following case history of a card file to be used for bibliographic purposes.

The development of an extensive bibliography in geochemistry made it necessary to design an edge-punched card small enough to manipulate easily, inexpensive, and simple enough to be searched by inexperienced personnel with a minimum of instruction. The card, moreover, had to be large enough to permit abstracts to be typed or cemented onto it, and versatile enough to be of real value to as many as five other groups in the same laboratory. After discussing the matter with interested colleagues, it was found that the McBee Company was able to furnish a standard card, $6\frac{5}{8}'' \times 7\frac{1}{2}''$, that met the stated requirements. A satisfactory compromise was reached between size of card and number of holes available for punching by having five, instead of the usual four, holes per inch. A double row of holes around the entire perimeter of the



A. Louis
No. 54

B. Breger
No. 10

FIG. 3. Notation of author. A. Louis (No. 54 in Table 2); shallow punches 4 and 1 in the tens field for complex number 5, and deep punch 4 in the units field for simple number. B. Breger (No. 10 in Table 2); deep punch in the tens field indicating the simple number 1, and zero punch.

card permitted maximum use. The card, designed for use by geochemists, spectroscopists, mineralogists, and analytical and inorganic chemists, is shown in Figure 1.

The section reserved for designation of author in the upper right-hand corner of the card (Fig. 3) has already been discussed. As pointed out, this numerical breakdown (shown in Table 2) permits but one author to be designated on a card. Any attempt to code more than one author will result in an ambiguous situation where combinations of the punches might represent authors having no relationship to the paper at hand. When a paper with coauthors is to be entered on a card, several alternate procedures are possible: (1) code the senior author; (2) code the author personally known or known

to be responsible for the continuous nature of the work; or (3) if both authors are equally well known, code the card for one author and make a second card with the minimum of cross-reference data but coded for the other author. The last situation, requiring two cards for reference, is rare.

The method of designating the year in which a paper appeared has also been discussed (Fig. 4).

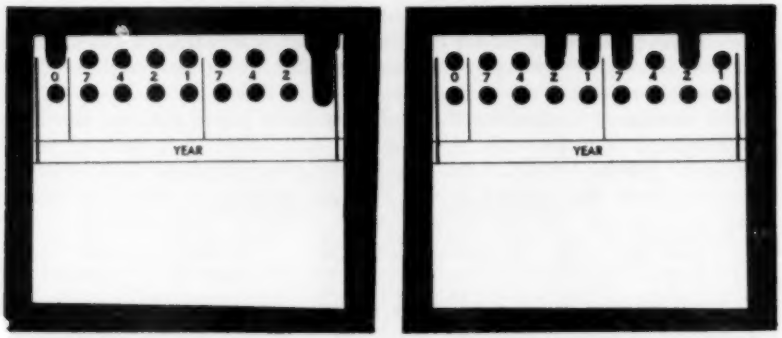
TABLE 2

NUMERICAL BREAKDOWN FOR CODING AUTHOR [1]

Aa to Al	01	Haa to Hak	35	Pa to Pd	67
Am to Aq	02	Hal to Haq	36	Pe to Pg	68
Ar to Az	03	Har to Hd	37	Ph to Pz	69
		Hea to Hem	38		
Baa to Baq	04	Hen to Hh	39	Qa to Qz	70
Bar to Bd	05	Hi to Hn	40		
Bea to Bem	06	Ho to Ht	41	Ra to Rd	71
Ben to Bh	07	Hu to Hz	42	Re to Rh	72
Bi to Bn	08			Ri to Rn	73
Bo to Bq	09	I to Iz	43	Ro to Rt	74
Bra to Brn	10			Ru to Rz	75
Bro to Bt	11	Ja to Jn	44		
Bu to Bz	12	Jo to Jz	45	Sa to Sch	76
				Scha to Schl	77
Caa to Car	13	Ka to Kd	46	Schm to Scht	78
Cas to Cg	14	Ke to Kh	47	Schu to Sd	79
Ch to Chz	15	Ki to Km	48	Se to Sg	80
Ci to Cn	16	Kn to Kq	49	Sh to Shz	81
Coa to Coq	17	Kr to Kz	50	Si to Sl	82
Cor to Cq	18			Sm to Sn	83
Cr to Cz	19	La to Ld	51	So to Sq	84
		Le to Lh	52	Sta to Std	85
Da to Dd	20	Li to Ln	53	Ste to Stm	86
De to Dh	21	Lo to Lz	54	Sto to Stz	87
Di to Dq	22			Su to Sz	88
Dr to Dz	23	Maa to Maq	55		
		Mar to Mb	56	Ta to Tg	89
Ea to El	24	McA to McF	57	Th to Tn	90
Em to Ez	25	McG to Md	58	To to Tz	91
		Mea to Meq	59		
Fa to Fh	26	Mer to Mh	60	Ua to Uz	92
Fi to Fk	27	Mi to Mn	61		
Fl to Fq	28	Mo to Mt	62	Va to Vz	93
Fr to Fz	29	Mu to Mz	63		
				Wa to Wd	94
Ga to Gd	30	Na to Nh	64	Wea to Weh	95
Ge to Gk	31	Ni to Nz	65	Wei to Wg	96
Gl to Gq	32			Wh to Wilk	97
Gra to Grh	33	Oa to Oz	66	Will to Wz	98
Gri to Gz	34				
				Xyz	99

[1] Courtesy McBee Keysort Co.

The section of the card marked "main element" was established for the use of spectroscopists or analytical chemists (Fig. 5). By punching the number 79, the atomic number of gold, in this field, it may be indicated that the abstract is concerned with an analytical technique for gold. Other elements designated by appropriate punches on the sides of the card might, for example, then indicate interfering elements.

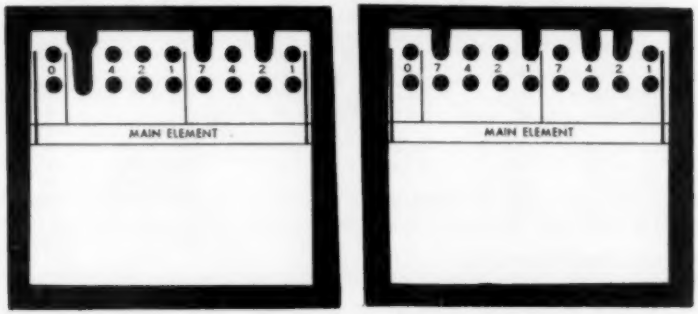


A. 1901 B. 1939

FIG. 4. Notation of year. A. 1901; B. 1939.

With a number of files, all using different codes but the same card, it seemed wise to allow for the isolation of cards should a mix-up inadvertently occur. This was accomplished by simply assigning a number to each file, in this case the number two.

The sides of the cards carry both elemental and numerical designations for each hole. When necessary, an element can be punched by direct coding. In those files not requiring elemental designation, the numbers can be used for direct coding, by either shallow or deep punch, of other information. As an example (Fig. 6), the punch reserved for lithium can also, as 23 shallow, be used to designate "oceanography," or as 23 deep, "mineral wax."



A. Gold B. Radon

Atomic number 79 Atomic number 86

FIG. 5. Notation of main element. A, Gold, atomic number 79; B, Radon, atomic number 86.

The entire bottom of the card has been left open for entries specific to any file being developed. It will be noted that space has been reserved for a 100-subject breakdown in the lower corner of the card (Fig. 7), and that the remainder has been set up for numerical coding should such be desired. In Figure 7 are shown several entries that demonstrate a number of points to be kept in mind when organizing a system. The subject, tar, recurs frequently and, for this reason, has been given an outer or shallow punch as indicated. The deep punch, on the other hand, has been reserved for the less frequently recurring subjects dealing with magnetism or ultrasonics. Because either of

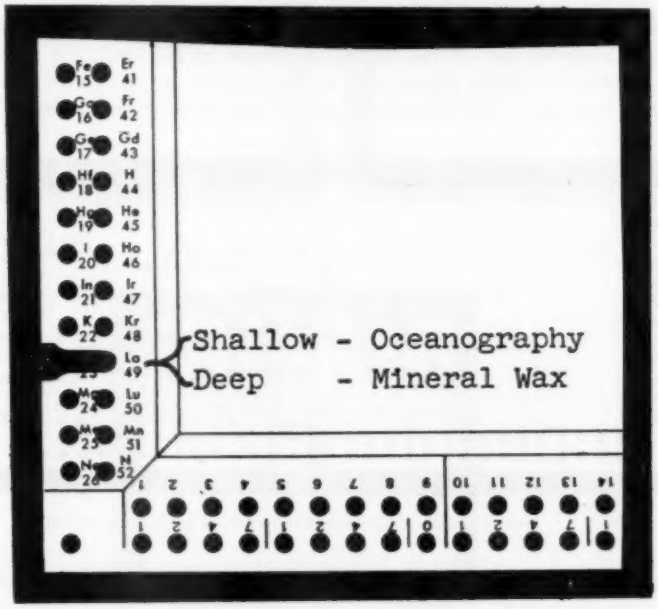


FIG. 6. Direct coding on side of card.

these subjects occurs infrequently, the two have been grouped and allotted but one punch. By so doing, a search of the overall file may lead to the isolation of perhaps 20 cards, some dealing with magnetism and some with ultrasonics. Although these cards will require isolation by hand sorting, the slight effort involved is well worth the space that would have been used had ultrasonics and magnetism each been allotted its own hole.

Referring to Figures 6 and 7, it is possible to demonstrate a search for a reference concerned with the use of ultrasonics in the isolation of mineral wax. Inserting the needles, one, two, or three at a time, in the holes designated in Figures 6 and 7, cards referring to "mineral wax," "isolation," "magnetism,"

and "ultrasonics" will drop from the deck. With very little effort it will then be possible to isolate and eliminate by hand-picking those cards dealing with "magnetism," leaving only the desired cards behind. The simplicity of this system merits primary consideration in setting up any file.

Should it be necessary to use a numerical breakdown with 99 subject entries, the technique is identical to that used for the "author" entry. Again it must be emphasized, however, that the 99 subjects must be mutually exclusive with no two occurring on the same card. Any attempt to code more than one number of the series of 99 will result in an ambiguous situation as demonstrated in Figure 8.

A great deal of information can be entered onto the card of Figure 1 by the use of both direct and numerical codes as indicated. Additional information can, however, be entered if other features of the card are employed. These advantages can be gained only at the expense or "calculated abuse" of the card or system. The following examples are presented in explanation.

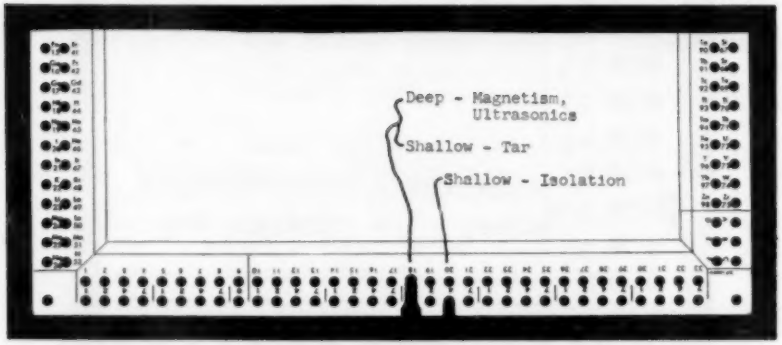


FIG. 7. Bottom half of card showing entries by direct coding.

The file under discussion was developed for the maintenance of a bibliography in geochemistry. Frequently a reference appears in which naturally occurring organic substances are related to various chemical elements, a situation in which it is desirable to use not only the subjects but also the elements direct-coded on the sides of the card. Although an attempt to apply two codes to the same series of holes usually leads to severe difficulty (see also Fig. 8), it has been possible to do so with a minimum of ambiguity as demonstrated in Figure 9.

The use of punches to designate direct-coded subjects is considered normal on the sides of the card of Figure 9. The designation by punches of the elements, symbols for which are printed on the sides of the card, is considered abnormal. Should a reference, such as that of Figure 9, occur for which it is necessary to code both subject and element on the sides of the card, it must be indicated that such an abnormal situation exists. Punching the hole desig-

nated by the arrow in the upper left-hand corner of the card shows that one or more elements are coded along the sides.

Use of a complex system such as this depends upon whether the search is for information for a particular element, or for information on a subject. If data for copper were desired, then the deck could be first sorted for those cards

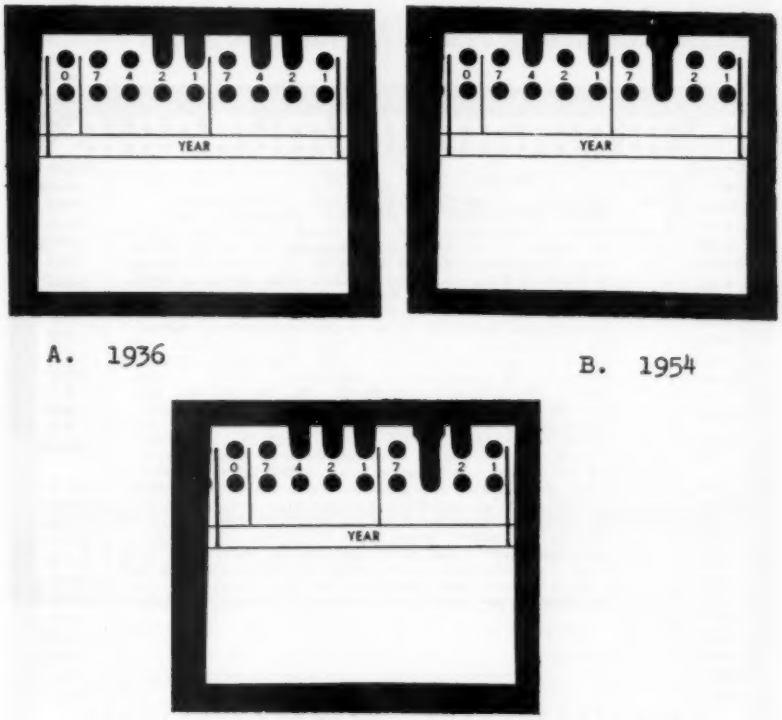


FIG. 8. Notation of year. A. 1936, B. 1954, C. 1936 and 1954. A and B are unambiguous; when the file is searched, C will fall when the tens field is searched for 30, 50, or 60, and the units field is searched for 3, 4, or 6. Possible dates for card C become 1933, 1934, 1936, 1953, 1954, 1956, 1963, 1964, or 1966. By noting two dates in the same fields, seven extraneous years are represented.

punched as shown by the arrow of Figure 9; the cards which fell would then be sorted for those punched "Cu" (the symbol for copper). In the direct code, a hole punched in item 13, also the punch for copper, would lead to the isolation of cards referring to humic acids. Because some cards might be punched for copper, it is clear that a mixture of desired and extraneous cards would

fall. Although a system such as this leads to the isolation of a number of cards that must be sorted by hand, it has the great advantage of doubling the number of entries that can be made on the sides of the card. This technique offers an example of a "calculated abuse" of the functions of the card, but the compromise between abuse leading to some hand sorting and the added number of possible entries is, in this case, clearly in favor of the latter.

Figure 10 illustrates an additional "calculated abuse" of this card, one which has proved extremely satisfactory in relating bibliographic studies to in-

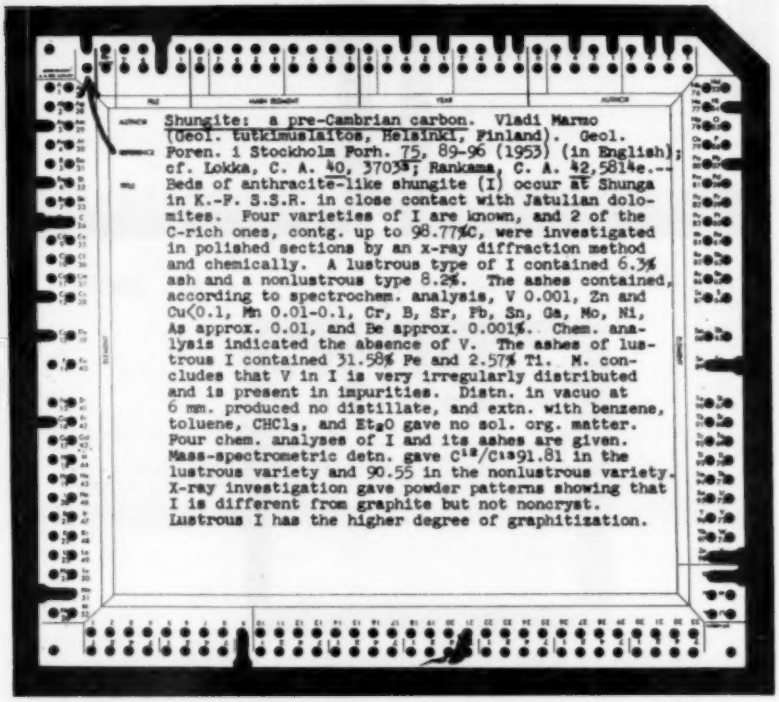

Shungite: a pre-Cambrian carbon. Vladi Marmo (Geol. tutkimuslaitos, Helsinki, Finland). Geol. Foren. i Stockholm Forh. 75, 89-96 (1953) (in English); cf. Lokka, C. A. 40, 3703⁵; Rankama, C. A. 42,5814e.--
Beds of anthracite-like shungite (I) occur at Shunga in K.-F. S.S.R. in close contact with Jatulian dolomites. Four varieties of I are known, and 2 of the C-rich ones, contg. up to 98.77%C, were investigated in polished sections by an x-ray diffraction method and chemically. A lustrous type of I contained 6.3% ash and a nonlustrous type 8.2%. The ashes contained, according to spectrochem. analysis, V 0.001, Zn and Cu<0.1, Mn 0.01-0.1, Cr, B, Sr, Pb, Sn, Ga, Mo, Ni, As approx. 0.01, and Be approx. 0.001%. Chem. analysis indicated the absence of V. The ashes of lustrous I contained 31.58% Fe and 2.57% Ti. M. concludes that V in I is very irregularly distributed and is present in impurities. Distn. in vacuo at 6 mm. produced no distillate, and extn. with benzene, toluene, CHCl3, and Et2O gave no sol. org. matter. Four chem. analyses of I and its ashes are given. Mass-spectrometric detn. gave C12/C13 91.81 in the lustrous variety and 90.55 in the nonlustrous variety. X-ray investigation gave powder patterns showing that I is different from graphite but not noncryst. Lustrous I has the higher degree of graphitization.

FIG. 9. Punched card illustrating the simultaneous use of two codes on sides.

formation readily available in files. The hole marked "reprint" in the upper left-hand section of this card is punched to show that a copy of the paper referred to on the card is available in the author's file. Reprints of technical papers or data, as received, are cemented into file folders, numbered consecutively, and filed according to number. The number of the folder is then noted on the related card (Fig. 10).

For ease in locating references, the entire card file has been stored alphabetically with respect to author. Although it is recognized that a feature of

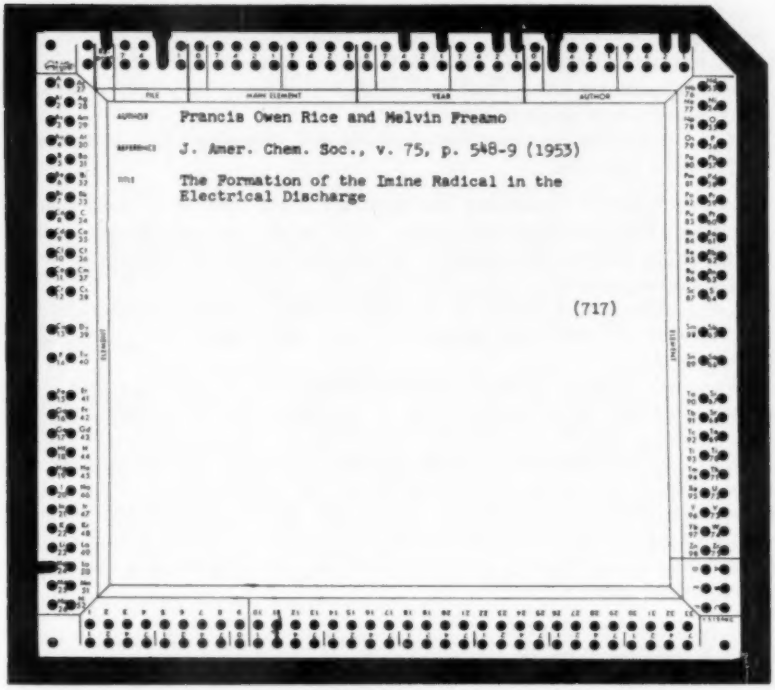

Francis Owen Rice and Melvin Freamo
J. Amer. Chem. Soc., v. 75, p. 548-9 (1953)
The Formation of the Imine Radical in the Electrical Discharge
(717)

FIG. 10. Card illustrating method of recording reprints.

edge-punched cards is the ability to store them in indiscriminate order and yet to extract desired information, alphabetical storage permits rapid determination of (1) work done by a particular author, and (2) any results of his work readily available in reprint form.

SETTING UP THE FILE

Experience has shown that by following certain simple paths it is possible to establish a punched card filing system requiring minimum revision.

(1) Analyze approximately 100 items of the type for which the system is being designed to establish their relative importance and relationships to each other. In determining the subjects to be coded, care must be exercised to prevent the choice of specifics; it is of much greater importance to itemize ideas which can be used together. For example, the two subjects, "ultraviolet light" and "lignin," if coded separately, can be combined to indicate the effect of ultraviolet light on lignin, or the use of ultraviolet light in the analysis of lignin. It would obviously be wasteful of peripheral space on the card to code these last two specific subjects when they may occur only rarely. By noting "ultra-

violet light," however, that subject may be used to modify any other subject on the card.

(2) Assign direct coded punches to major interests that recur frequently. Conserve space by using numerical codes for subjects only one of which is likely to occur in a single reference.

(3) Provide for the expansion of a code with changing interests by reserving holes for later use.

A punched card system can be a great aid in the solution of many types of problems. For statistical information, it is possible to code ranges of data; for inventory systems it is possible to note the number of cases of a certain item, its brand, and cost data; a bibliographic example has already been cited. Use of punched cards cannot be universally recommended, however, because for many simple reference systems ordinary, inexpensive cards will suffice equally well.

Punched cards will provide only that information coded by the user; to be assured that desired information may be available, the user should punch all information (other than standard subjects such as year or author) himself.

Each punched card filing system will depend upon the specific requirements to be met. For this reason an infinite variety of possible courses suggest themselves when a new system is considered. It is hoped that the foregoing discussion of limitations and techniques will aid the novice in getting started; beyond that point the only limitations are the cards themselves and the ingenuity of the user.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C.,
Oct. 23, 1957

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Economic Geology
Vol. 53, 1958, pp. 339–351

DISCUSSIONS

ORE GENESIS—THE SOURCE BED CONCEPT

Sir: The Source Bed Concept as proposed by Knight (ECON. GEOL., v. 52, no. 7, p. 808–817, 1957) is based on the observed fact that a number of the world's sulfide deposits show preference for a particular stratigraphic horizon within a given field. From this, Knight concludes that most, if not all, sulfide orebodies are "basically sedimentary" in origin.

In order to become a Source Bed Conceptionist, Knight shows that one must depart from the observed fact and cling tenaciously to the required conclusion for the duration of the investigation. For example, on page 814, Knight quotes Gill's general description of the ore deposits of the Canadian Shield and follows with the announcement that "There is, in this statement, a strong suggestion of stratigraphic control on a regional scale." It would be more accurate, but less in line with the Source Bed Concept, to say instead: "This description states that ore deposits of the Canadian Shield are observed to commonly occur in weakly metamorphosed volcanic and sedimentary rocks."

On page 815, Knight states as follows:

> If the ore-bearing bed were invariably the one rock type it might be argued that the chemical properties of the bed were responsible for its favorability to ore replacement. This however is not the case. Each of the common sedimentary rocks with the exception of greywacke, namely shale siltstone sandstone conglomerate limestone dolomite and marl, comprises the ore-bearing bed in different fields. The author finds the popular epigenetic theory unacceptable for these fields.

One understands from the above that a variation in the type of host rock in different fields argues for a syngenetic origin because chemical control cannot be operative in a multitude of environments. If one submits to this hypothesis, it follows that a widespread similarity of mineralized rock types speaks against the syngenetic theory. However, a few paragraphs later, one is confronted by the following statement:

> Detailed stratigraphic environment is described for only a few of the deposits but, of the 108 for which the country rock is cited, 56 are actually in limestone or dolomite and a further 7 have these rocks in the immediate vicinity.

Is one entitled to inquire whether this last statement has been made in a rush of good-fellowship to give the epigeneticists a fighting chance or whether it, too, has somehow been construed as evidence for the Source Bed Concept?

Guided by the principle that the wider the application, the more powerful the theory, Knight comes to the following conclusion:

> If the orebodies of the fields listed in this paper are basically sedimentary in origin, then it is logical to argue that *all* sulfide orebodies, with the possible exception of

some magmatic segregations, were derived from original sedimentary accumulations of sulphides. . . .[1]

It hardly need be stated that the listing of a few epigenetic sulfide deposits (e.g., Cerro de Pasco, Cornwall, Butte, Cripple Creek, Noranda, Potosi, Braden, Llallagua, etc.) followed by the comment that *all* other sulfide deposits must be epigenetic would be equally illogical. Knight's insertion of the words "possible" and "some" before "magmatic segregations" provides evidence of the tenacity with which he clings to the sedimentary origin and actually suggests that, while some magmatic segregations are derived from magmas, other magmatic segregations are doubtless derived from sediments!

Positively stated opinion does not lend credence to scientific communication. On the contrary, it seems to the present writer that unsubstantiated generalities are more easily digested, if not assimilated, when modified by such words as "maybe" and "perhaps."

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Jan. 20, 1958

THE SOLUBILITY OF SOLIDS IN GASES

Sir: G. W. Morey's excellent paper in the May, 1957, issue of ECONOMIC GEOLOGY will probably remain a standard work in this interesting field for some time. For that reason we wish to point out a possible error, not in the presentation of the facts, but in the degree of certainty of the hypothesis that some silicate-water systems must show two critical end points when considered as simple two component systems. The gas-liquid terminology used by Morey we will preserve for the present; but Morey's definition of "gas" and rejection of the term "fluid phase" are not satisfactory to us for reasons that will appear later.

The theoretical model of a two-component system considered in pressure, temperature and composition presented by Morey is highly idealized through a number of simplifying assumptions. The chief of these are: (i) that the behavior of the system can be expressed by such a two-component model, i.e., the system is truly binary (ii) that the solid phases are completely immiscible (iii) that all other phases are completely miscible. With these assumptions, two cases are realized; Case I, in which the projection to the P-T plane of the three overlying three-phase curves $(B + L + G)$ is not intersected by the projection of the critical plait-point curve $(L = G)$; and Case II, in which intersection of these projections results in two critical end points p and q. Now, although a simplified model is the reasonable first step to arrive at understanding of the complexities of silicate-water systems, we wonder if the third assumption is fully justified; specifically, we question the assumption that a miscibility gap in the saturated liquid solution (or melting) surface does not arise as a complication. Niggli (1937, p. 253) briefly considered

[1] Present writer's italics.

the possibility of such immiscibility in systems of geological interest, but dismissed it largely for lack of evidence and on geological grounds, so that he did not develop fully the possible diagrams. Nevertheless, he recognized possible geologic importance of fluid immiscibility at high pressures. Discussion of the problem has also been taken up by Nikolaev (1955), whose Type III diagram seems to have been developed in much the same way as our proposed Case IV.

The consequences of an assumption of a miscibility gap in the saturated solution (or melting) surface of the hypothetical model and projections derived therefrom had been worked out by us prior to publication of Morey's paper and will be formally presented as soon as detailed diagrams can be drawn up.

Two more cases, Case III and Case IV, are recognized. In Case III, which is somewhat analogous to Case I, the miscibility gap is realized at moderate pressures without interference of critical conditions of the $(L = G)$ transition, exactly in the way suggested by Morey (1949). In Case IV, on the other hand, the surface representing the composition of saturated liquid solutions (or melts) is penetrated at a relatively low pressure by the critical plait-point curve in a way analogous to Case II. But, in Case IV, penetration takes place before the miscibility gap is realized in isobaric sections; that is, before the condition of "melting under the solvent" $(B + L_1 + L_2)$ develops. This does not, however, bar the possibility of a miscibility gap appearing at high pressure, as Niggli (1937) pointed out.

In Case IV, therefore, a point identical with the p point of Case II is developed; but a point similar to q may or may not be realized depending on the way in which the previously considered plait $(L = G)$ and three-phase curves $(B + L + G)$ are related to an additional critical plait-point curve (consolute line) $(L_1 = L_2)$ and three-phase equilibrium curve $(B + L_1 + L_2)$.

Within our model, then, exist two critical plait-point curves, one the transverse plait $(L = G)$, the other the longitudinal plait $(L_1 = L_2)$, and also three sets of three-phase equilibria $(A + B + L)$ $(B + L + G)$ $(B + L_1 + L_2)$ each made up of three lines. The low-pressure part of the model, where $(A + L + G)$ would exist, is not worth considering for our present purposes. All of these curves can be considered stably or metastably as shown in Figures 1, 2, 3, and 4 drawn to be compared with Morey's Figure 2 (p. 229).

The longitudinal plait (consolute line) $(L_1 = L_2)$ might rise or fall in temperature with increasing pressure. The curve $(B + L_1 + L_2)$ will probably behave like the melting point line $(B + L)$ and lie nearly parallel to it in P-T projection, at least at high pressures.

Two additional intersections of particular importance to be considered in deriving Case III and Case IV models from Case I and Case II are: first, intersection of the three phase line $(B + L + G)$ with three phase line $(B + L_1 + L_2)$; and second, the intersection of the plait $(L_1 = L_2)$ with plait $(L = G)$. In Case III the first intersection gives the quadruple point Q,—$(G + L_1 + L_2 + B)$ and thence, after cross-over, the three phase lines $(L_2 + L_1 + G)$ and $(B + L_1 + L_2)$ as described by Morey (1949) and now shown in our Figure 1. An additional possibility is the intersection of

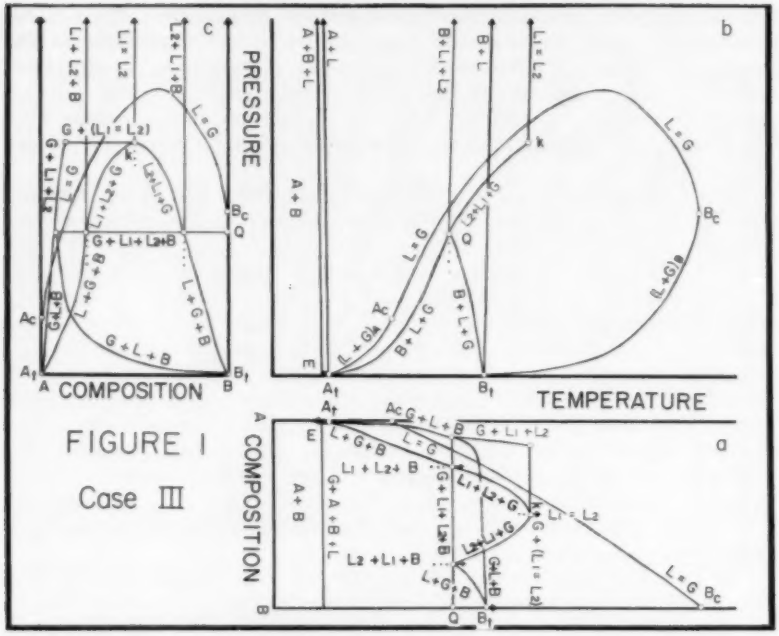

FIGURE 1

Case III

FIGS. 1, 2, 3 and 4. Projections of a hypothetical solid pressure-temperature-composition model of two components A and B $(A + B = 100\%)$. A is more volatile than B; solid phases (A and B) are completely immiscible; liquid phases (L) show a miscibility gap $(L_1 + L_2)$; gaseous phases (G) are completely miscible and zeotropic. Three phase lines $(B + L + G)$, $(B + L_1 + L_2)$, $(A + B + L)$; two phase lines of one component $(A + L)$, $(B + L)$, $(L + G)_{A,B}$; and critical plait-point curves $(L = G)$, $(L_1 = L_2)$ are projected, in that part of figure marked "a" to isobar, in that part marked "b" to isopleth, in that part marked "c" to isotherm. Solid lines show stable realization of curves, dotted lines show unlikely realization metastably. Where possible, the first letter of a combination written along a line states the phase represented by the line. Points At, Bt, Ac, Bc denote triple points and critical points of A and B, respectively. E marks the eutectic $(A + B + L + G)$; k and p are critical end points; Q is the quadruple point $(B + L_2 + L_1 + G)$.

FIG. 1b. Critical curve $(L = G)$ is uninterrupted between Ac and Bc. Three phase line $(B + L + G)$ connecting E to Bt is interrupted by three phase lines $(B + L_1 + L_2)$ and $(L_2 + L_1 + G)$ at quadruple point Q. Three phase line $(L_2 + L_1 + G)$ is interrupted by critical curve $(L_1 = L_2)$ at critical end point k,—$G + (L_1 = L_2)$.

$(L_1 + L_2 + G)$ with $(L = G)$, giving one critical end point, k,—$(L_2 + L_1 = G)$, as shown in Figure 2. No other critical end point can be generated as long as the possibility of liquid immiscibility holds, and an impossible abrupt end of the critical plait-point curve $(L = G)$ can only be evaded if this transverse plait swings into the longitudinal plait $(L_1 = L_2)$. In Case IV,

however, part of the lower branch of the three phase curve $(B + L + G)$ becomes unstable because of intersection with the plait $(L = G)$ at the p point, and the intersection of the two three-phase lines $(B + L + G)$ and $(B + L_1 + L_2)$ is no longer realizable as a quadruple point. The result is that $(B + L + G)$ swings into $(B + L_1 + L_2)$ without a critical end point. Intersection of the plait point curves $(L = G)$ with $(L_1 = L_2)$ likewise causes

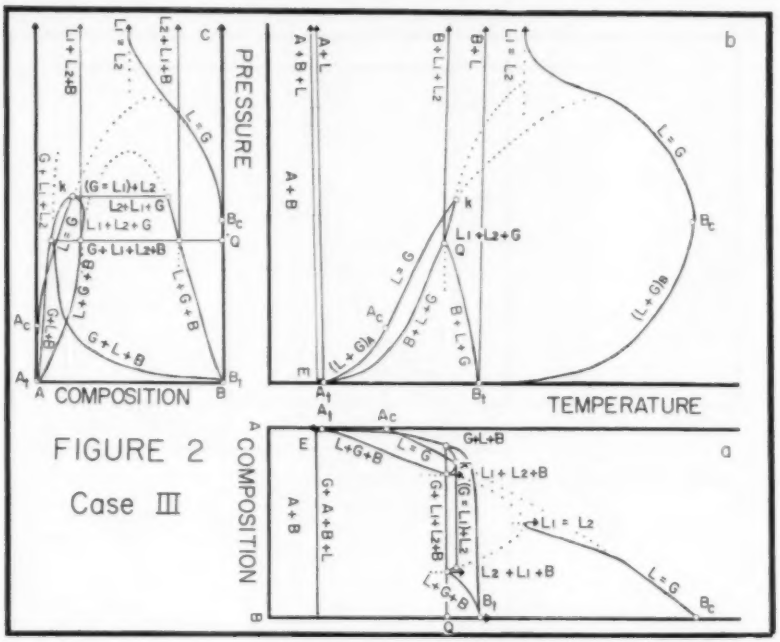

FIG. 2b. Critical curve $(L = G)$ rising from Ac intersects three phase curve $(L_1 + L_2 + G)$ rising from Q at critical end point k,—$(G = L_1) + L_2$. Upper branch of critical curve $(L = G)$ followed from Bc turns into the critical curve (consolute line) $(L_1 = L_2)$.

In Figure 2a the three phase equilibrium $(L_2 + L_1 + G)$ cannot be lettered for lack of space.

a swing in the direction of that plait without a critical end point as shown in Figures 3 and 4, leaving only one critical end point p.

The general relationships shown in Morey's Figure 13, and also the course of the three-phase line of the albite-water system (Bowen and Tuttle, 1950) are to be expected from this consideration of Case IV; and, further, in this analysis, no upper (q) critical end point need be expected at very high pressures. This is because intersection of the two plaits $(L = G)$ and $(L_1 = L_2)$ has turned the transverse plait into the longitudinal plait (the former becoming unstable at high pressure) and theoretical necessity of the

second intersection (q) of the transverse plait ($L = G$) with the three-phase curve ($B + L + G$) disappears in reality.

Intersection of the transverse and longitudinal plaits with consequent swing in direction of the critical plait-point curve affords explanation of the course of this curve after it leaves Bc in a few systems in which it has been followed experimentally. For example, in some systems (notably N_2-SO_2) the critical plait-point curve falls in temperature before reversing and rising with increase

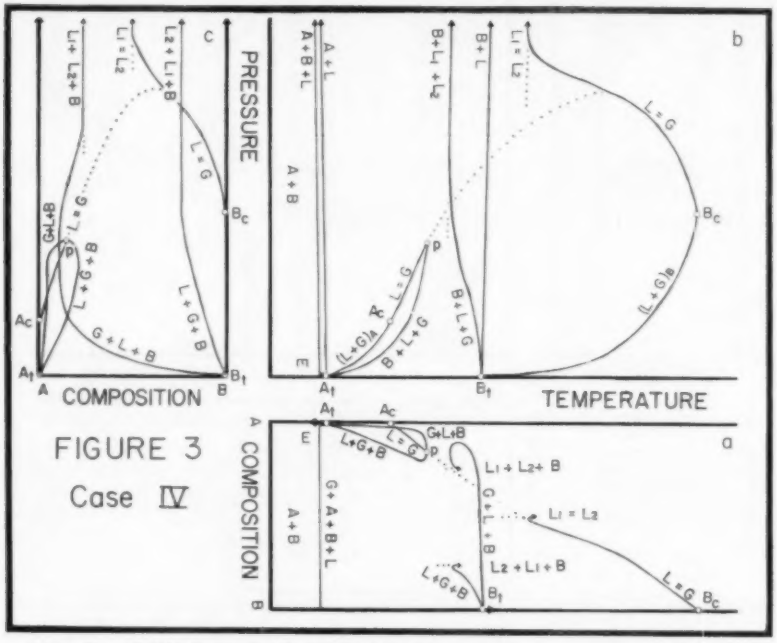

FIG. 3b. Critical curve ($L = G$) rising from Ac intersects three phase curve ($B + L + G$) rising from E at critical end point p,—($L = G$) + B. Upper branch of critical curve ($L = G$) followed from Bc turns into consolute line ($L_1 = L_2$), the temperature decreasing to a minimum and then rising with increasing pressure. Three phase curve ($B + L + G$) turns into ($B + L_1 + L_2$) probably descending to a minimum temperature and then rising with increasing pressure.

of pressure; in others (notably He-NH_3) there is a continuous increase in temperature with increase in pressure. A hypothetical example of a system of the first type, considered in the light of Case IV, is shown in Figure 3, where the ($L = G$) curve may be followed downwards from Bc until it intersects the ($L_1 = L_2$) curve rising in temperature with increasing pressure. In the second type, shown similarly in Figure 4, the rising ($L_1 = L_2$) curve intersects the ($L = G$) curve very shortly after it leaves Bc.

It is possible, on the other hand, that the ($L_1 = L_2$) curve descends in

temperature with increasing pressure after being realized stably by intersection with the $(L = G)$ curve so that eventually the intersection of $(L_1 = L_2)$ and $(B + L_1 + L_2)$ is realized as a critical end point. A situation practically indistinguishable from Case II might then be realized; except that the upper critical end point q might be at very high pressure, and could possibly lie in temperature below the p point if the line $(B + L_1 + L_2)$ descends far enough in temperature with increasing pressure. Possibly, however, a minimum is reached on $(B + L_1 + L_2)$ as we show in our figures.

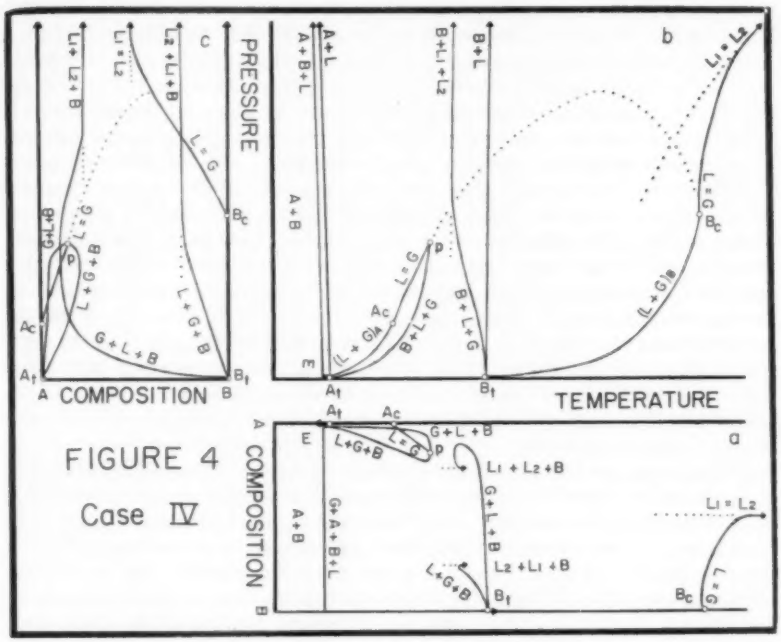

FIGURE 4

Case IV

FIG. 4b. Critical curve $(L = G)$ rising from Ac intersects three phase curve $(B + L + G)$ rising from E at critical end point p,—$(L = G) + B$. Upper branch of critical curve $(L = G)$ followed from Bc turns into consolute line $(L_1 = L_2)$ with progressive rise of temperature with increasing pressure. Three phase curve $(B + L + G)$ turns into $(B + L_1 + L_2)$ as shown in Figure 3b.

Distinction of Case IV (with descending $(L_1 = L_2)$ curve at high pressures) from Case II is at present almost impossible, and there is little experimental evidence to support the reality of the relationships for Case IV apart from the negative evidence that it seems difficult to reach a q point in silicate-water systems. Some theoretical and geological considerations, however, point to the possibility of immiscibility of silicate melts with watery solutions, as Barth and Rosenquist (1949) and Shand (1944), among others, have sug-

gested. Part of Niggli's (1937) objections, therefore, are not so persuasive as they once were.

Case II is not entirely satisfactory as an explanation either, for the available experimental evidence indicates that, if Case II describes the behavior of water-silicate systems, it must be assumed that the critical plait-point curve of $(L = G)$ transition must rise to very great pressures from the probable relatively low critical pressures of silicates expectable from their low vapor pressures. This too, is in spite of the fact that the assumed complete miscibility of gaseous and liquid phases would indicate a simple addition of properties; so that p and q might be expected to lie approximately linearly between the values of Ac and Bc, as they do in the system ether-anthraquinone.

If Case IV is generally accepted as an explanation for the lack of q point, then the term "fluid immiscibility," inherent in the assumption of setting up the model, becomes necessary at high pressure in place of "liquid immiscibility" possible at low pressure. The only alternative is "gaseous immiscibility" which suggests a revision of our concepts of the behaviour of gases.

The term "fluid phase" is a good one, and should be applied wherever there is doubt about the state, as Ricci (1951, pp. 95 and 183) points out. For example, in the solid model of a binary system, considered in temperature, pressure and composition, there is a large volume of space representing the state and composition of unsaturated solutions. This volume is continuous throughout the model, yet in some parts of it the fluid would, from the common-sense point of view, be called liquid, and, in others, gas. These parts can be separated only by arbitrary definitions which have not yet been satisfactorily drawn. In our opinion, it is better to refer to this volume as the continuous fluid field, which becomes more and more obvious in isobaric sections at higher pressures.

Presumably, to test for a gas as defined by Morey, it would be necessary to carry out a continuous isothermal expansion to zero pressure without a phase change of the sort that one would call a liquid-to-gas transition. In models for all four cases, this definition puts the upper temperature limit of the liquid-to-gas transition along the maximum temperature line on the vaporus surface, and not along the critical plait-point curve—which depends on the identity of composition $(L = G)$. Arbitrary division of the continuous fluid field by imaginary isothermal extension of the critical plait-point or other curve towards higher pressures to sweep out a dividing surface seems to us rather pointless, since such a surface has no physical significance.

The state of a phase as gas or liquid can be defined unambiguously, then, only when the phase is part of a two-phase or three-phase equilibrium; that is where temperature, pressure and composition of the phase are represented on one of the two-phase surfaces, or on a three-phase line. It is further necessary to separate the two-phase surface from others by a line, which, for the gas-liquid equilibrium in Case I, would be the critical plait-point curve and extensions from it along the boiling curves of the pure components passing through the triple points and joined (at low pressure) by the gas and liquid compositions of the three phase curves $(B + L + G)$ and $(A + L + G)$. Between p and q points in Case II, however, the dividing line cannot be drawn

between vaporus and liquidus surfaces; and no satisfactory convention exists for the definition of the state of the fluid in this case, beyond an assertion that it is gaseous according to an arbitrary definition of a gas. But arbitrary definitions of a gas usually given, as, for example, that reiterated by Morey, are neither satisfactory for general application in the space model, nor for comprehension of the phase changes going on in natural silicate systems deep in the earth.

Use of the term "gas" for the high pressure phase richer in the more volatile component has led to a great deal of confusion, since it is assumed that such a "gas" must "condense" to a liquid with consequent violent changes of solubility—geological literature abounds with examples. Such "condensation" actually is only a matter of nomenclature; the name of the phase changing from "gas" to "liquid" on crossing a line or plane extended in imagination from some critical temperature and in reality lacking physical significance, at least, as far as solubility is concerned. The "gas" on the upper branch of the three-phase curve will, on cooling and decompressing geothermobarically, most likely pass well to the high-pressure side of p and will become a "liquid" without undergoing condensation. Development of a gaseous phase, recognizable in the common way, however, would be possible (with a steep geothermal gradient) if the fluid crossed the stable part of the lower branch of the curve $(B + L + G)$. Pneumatolysis, in the original sense defined by Bunsen would then occur, this being the common process in fumaroles.

We prefer to retain "fluid" as a useful term to separate phases from the solid without the need of being specific as to gas or liquid. It is very useful to describe fluid immiscibility in Case IV, following the concept of the continuous fluid field. But we do not apply the concept of fluid immiscibility to obvious liquid-gas equilibria in Case I and Case II where liquidus and vaporus surfaces can be clearly separated by the critical plait-point curve, and unambiguous definitions of the state can be given. We feel, however, that Case IV is a more general case, and that if the upper three-phase line is to be defined as $(B + L + G)$ rather than $(B + Fl_1 + Fl_2)$—which we prefer to $(B + L_1 + L_2)$—then it must be shown in which case the system belongs by either continuous traverse of one of the three-phase curves or critical plait-point curve, or by location of both p and q points.

Otherwise it is simpler to assume Case IV and an equilibrium $(B + Fl_1 + Fl_2)$.

A further criticism of the model, as presented, can be aimed at the first assumption, namely that the behavior is truly binary. Certainly, in natural silicate-water systems the multiplicity of components will make it very unlikely that three-phase behavior can be represented along a line projected to a T-P plane. The three-phase behavior will extend over a temperature and pressure interval, no doubt between limiting curves. This consideration, and considerations of the extent of the three-phase line over a wide range of pressure in experimentally determined systems of silicate-water type, seem to indicate that many natural silicate systems are very likely eventually to reach this upper three-phase condition if they are moved a sufficient distance along a geothermobaric gradient. In the three-phase condition, silicate crystals are

in equilibrium with two sorts of fluid, one of which might be regarded as magmatic and the other hydrothermal. The latter will have the much greater penetrating power usually associated with the gaseous phase. (We reject the term "pneumatolytic" for this phase on the grounds given above.) Growth of silicate crystals would not then be limited to the magma chamber, but might extend far beyond, with the possibility that this situation might exist over a wide temperature-pressure interval.

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THE SOLUBILITY OF SOLIDS IN GASES

Sir: I have read the preceding discussion by F. G. Smith and R. E. Jones of my article that appeared in the May issue of 1957. I have little criticism of it. However, I think that it is clear that I did not intend to write a treatise on binary systems with a volatile and a non-volatile component. I was trying to bring together the available information on the solubility of solids in gases, and only included that minimum of theory necessary for discussing that information.

A complete discussion of the relationship in systems containing volatile and non-volatile components should consider the complications caused both by the formation of compounds and of two liquid layers; the occurrence of critical end-points of the type $(G = L)$ and $(L_1 = L_2)$; cases of liquid immiscibility in which the quadruple point $G + L_1 + L_2 + S$ is missing; the cases in which the gas phase is either richer in the more volatile component than either liquid, or intermediate between them; and the complications caused by the critical curve joining the critical points of the two components having

either a maximum or a minimum. Any treatment of these topics must be based on the pioneer work of van der Waals (Lehrbuch der Thermodynamik, van der Waals-Kohnstamm, 1908) and subsequent papers by his pupils and followers, especially Scheffer and Büchner.

The footnote on p. 227, "Complications caused by the formation of immiscible liquids are omitted from consideration," did not imply that I consider these unimportant. I agree with Dr. Smith that unmixing in systems containing water may be important. It is the most probable explanation of the phenomena found with water and Na_2SO_4, K_2SO_4, Li_2SO_4, $Na_4P_2O_3$, and Tl_2SO_4 [Morey and Chen (J. Am. Chem. Soc., 78, 4249–52, 1956)] as they stated in their paper. The obvious possibility of an apparently two component system becoming more complex owing to decomposition must, of course, always be kept in mind. Morey and Chen did not find decomposition with the above sulfate systems, but Morey and Hesselgesser did find it with sodium silicate, and with albite and orthoclase (ECONOMIC GEOLOGY, 46, 821–835, 1951). In the same paper Morey and Hesselgesser found no evidence of decomposition of several sulfides with H_2O at 500° C, 15,000 psi, but pyrite was decomposed with formation of pyrrhotite.

I am not greatly interested in the semantic discussion of gas or fluid. Personally, I have often found "fluid" used in a way I found confusing, but others may not. It is of interest to note that Kritchevsky and Zielis (Acta Physicochimica U.R.S.S., 18, 264, 1943) found coexistence of two immiscible gases.

GEORGE W. MOREY

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C.,
Dec. 19, 1957

FACIES RELATIONS IN THE GUNFLINT IRON FORMATION—A REPLY

Sir: In a recent discussion of the writer's paper on the Gunflint iron formation, E. A. Alexandrov (2) questions the evidence for, and adequacy of a volcanic source for the iron and silica contained in the formation. He favors instead a chemical weathering source with ensuing transportation of ferric iron followed by reduction to ferrous iron with the aid of organic matter. Alexandrov (1) recently presented admirably the details of this proposed method of origin of banded iron formation. The writer does not question the feasibility of such an origin under actualistic conditions. However, field evidence suggests to him that the Gunflint iron formation did not, in fact, have this origin. Since the genesis of banded iron formation is an important aspect of Precambrian geology it seems worthwhile to elaborate briefly on this point.

In commenting on the absence of any sign of weathering in the basement rocks with the exception of local mild decomposition, Alexandrov suggests that the weather part of the underlying rock was easily eroded and carried away into deeper parts of the basin. In this connection, the writer had occasion

to examine this past summer for the first time an exposure of Gunflint basal conglomerate and chert near Slate Island east of Rossport on the north shore of Lake Superior. The conglomerate is exposed along the shoreline for 500 feet and ranges up to 10 feet thick. It is composed of semi-rounded to rounded boulders and pebbles of greenstone and granite in a gritty matrix. Sorting is extremely poor, adjacent fragments ranging from gravel size to boulders 4 feet in diameter. The conglomerate, with respect to distribution, composition, size and sorting closely resembles present beach accumulations on the shore of Lake Superior where relief and wave action are considerable. Of particular significance, isolated, fresh orthoclase crystals with lustrous cleavage faces are present in the matrix of the conglomerate. Similar fresh feldspar crystals are not uncommon at the surface of the basement granite throughout the length of the Gunflint formation (3, p. 570). Indeed, the fresh appearance of the basement rocks led T. L. Tanton to suggest glacial scouring immediately prior to Gunflint time. Such fresh condition of basement rocks, in conjunction with absence of lateritic material—the normal product of deep chemical weathering—in the Lake Superior region, seems difficult to reconcile with extensive chemical weathering.

Regarding the adequacy of volcanism to supply large quantities of iron and silica, Alexandrov examines contemporary hot spring and finds them lacking in magnitude. However, recent age determination on Gunflint material indicate an age of almost 2 billion years (4, p. 1304). This projects back to a stage of earth development wherein Lyell's theory of uniformitarianism must surely require modification in terms of magnitude, if not of principle. It is evident that contemporary phenomena of modest scale may well have operated on a vastly greater scale at the mid-point of earth's history. May this not apply particularly to volcanism and related activities?

Have Precambrian banded iron formations formed during specific controlling climatic conditions which were repeated at intervals of 600×10^6 to 750×10^6 years in different parts of the world as suggested by Alexandrov (1, p. 460)? Age determinations of Huronian-type iron formations in the Lake Superior region suggest a common age of 1700×10^6 to 2000×10^6 years. Sufficient time has thus elapsed for at least two and possibly three proposed recurrences favoring deposition of banded iron formation. Further age determinations on Huronian-type iron formations may demonstrate whether or not such has occurred. In the meantime, perusal of the geologic columns with respect to iron formations does leave some room for doubt.

In conclusion, however, it seems that the Gunflint formation with its variety of facies, unaltered mineral composition and plentiful outcrops not only provides unusual opportunity for detailed investigation of banded iron formation but at the present stage of investigation, also leaves considerable room for difference of opinion regarding genesis.

A. M. Goodwin

Algoma Ore Properties, Limited,
Jamestown, Ontario,
Jan. 20, 1958

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4. Tyler, S. A., Barghoorn, E. S., and Barrett, L. P., 1957, Anthracite coal from Precambrian Upper Huronian black shale of the Iron River district, Northern Michigan: Geol. Soc. Amer. Bull., v. 68, no. 10, p. 1293–1304.

Economic Geology
Vol. 53, 1958, pp. 352–362

REVIEWS

Mineral Commodities of California. Prepared under the direction of OLAF P. JENKINS; edited by Lauren A. Wright. Pp. 736; figs. 130; maps and cross-sections, 138; photographs, 239. California State Division of Mines, Bulletin 176. San Francisco, California, 1957. Price $7.50.

There is no more pragmatic test of the value of any publication than the appearance of a new edition. By the same token, the appearance of a new edition is always a matter of special interest: has the material been brought up to date, has it been improved, expanded, condensed; or is it perhaps no more than a corrected reprint of the preceding edition?

"Mineral Commodities of California," appearing now as a revised edition of a work (Bulletin 156) under the same title, issued in 1950, provides a measure not only of the growing store of information on this subject, but of the growth and progress in the State organization that has made this notable publication possible. Both bulletins have the same title, both were authored by the same organization. There the resemblance largely ends. Bulletin 156 is an octavo volume of 443 pages; Bulletin 176, a quarto volume of 736 pages. Bulletin 156 weighs just one and one half pounds; Bulletin 176 weighs over five pounds. (Though it contains a wealth of interesting information it obviously has not been designed for bedside reading!). The index of Bulletin 156 carried some 1,400 listings; the index of Bulletin 176, more than 4,000. Best of all, whereas Bulletin 156 contains not a single geological map, Bulletin 176 is replete with geological maps *and* sections, many never before published. To be sure, not all of the 138 maps are geological maps; the majority are locality maps, and very useful too.

The organization of the present volume represents another improvement. Gone is the separation that was made in Bulletin 156 of mineral commodities into "Mineral Fuels," "Nonmetallic Industrial Minerals" and "Metals." In the new edition it was recognized that the virtues of such categories have largely disappeared, and all commodity chapters are now conveniently arranged in alphabetic order. A former chapter summarizing mineral production by counties has wisely been eliminated. Counties and county statistics doubtless have their political value; but in dealing with a subject so large and so important as the mineral industry of California, the over-all statistics of production—presented in numerous charts in the pertinent commodity chapters of the new volume—are of much greater value. Also eliminated has been a segregated directory of mineral producers, dealers and commercial laboratories. These useful data, in the new edition, are appropriately incorporated within the individual chapters. Forty-one of the 77 chapters (topics) in the new edition have been prepared by authors different from those who prepared the corresponding chapters in the preceding edition, and even in those instances where the same author has prepared the same topic, the chapter has been largely rewritten and up-dated. Ten of the chapters are new: Carbon dioxide, Minor metals, Natural-gas liquids, Nickel, Quartzite and quartz, Rare earth elements, Shale (expansible), Specialty sands, Thorium, Vanadium, and Wollastonite. Almost all treatments have been considerably expanded.

The present volume is an outstanding contribution to the literature of the mineral industries and deserves extensive review. Yet even to list the 77 chapter headings and the names of the 25 contributing authors (most of whom are on the staff of the Division of Mines) would expand this review unduly. Although the volumes serve different objectives, by way of providing a condensed yet impartial evaluation of the coverage that has been achieved, it will be of interest to compare the topics treated in this volume with those discussed in the latest (2nd) edition of Bateman's "Economic Mineral Deposits" (for the metals) and with those to be included in the forthcoming new edition of "Industrial Minerals and Rocks" (for the nonmetals). Bulletin 176 discusses (albeit with less emphasis on geology and somewhat more on processing and marketing) every metal in Bateman except tantalum, and to some it gives greater coverage. For example, rhenium gets three lines in Bateman, 32 lines in Bulletin 176. This no doubt results from the fact that although rhenium is not currently in commercial production in California, or anywhere else, it has become today an element of increasing interest to the high-temperature metallurgist. Every topic covered in "Industrial Minerals and Rocks" is covered in Bulletin 176 with the exception of two: Chalk and whiting, and Tripoli. Bulletin 176 gives chapter status to Bromine, Iodine, Shale (expansible), Rare earth elements, and Wollastonite—commodities not now slated for "top billing" in the Mudd volume. Conversely, several commodities scheduled for chapter treatment in the Mudd volume receive sub-head treatment in Bulletin 176. For example in Bulletin 176, slate is treated in the chapters on Dimension stone and on Crushed stone; bauxite is discussed under Aluminum; and potash under Salines. This last is somewhat surprising considering that potash salts are among our most important fertilizer minerals; that potash was a "critical mineral" during World War I; and that it is a commodity for which California is one of the two principal producing states. Incidentally even more surprising, in view of their importance as mineral products, is the absence of any reference in an otherwise very comprehensive index to "fertilizers" or "fertilizer minerals," or to "soil amendments" or even to "agriculture"—one of our important mineral consuming industries. The chapter on Granules in the Mudd volume finds no parallel in Bulletin 176, although the subject is discussed briefly in the chapter on Crushed stone. Even in the index of Bulletin 176 there is no citation either to granules or to roofing materials, despite that southern California is one of the major consuming areas for this commodity. Indeed the only way to discover that the subject is discussed is to look up the name of the principal producer (Minnesota Mining & Mfg. Co.) in the index and find there a citation to a photograph of their quarrying operation, within a few pages of which the text discussion can be located.

The treatment of each topic follows a consistent plan whereby, after a succinct introductory statement, there follow, in general, discussions of mineralogy and geology, locations in California, utilization, marketing problems and prices, mining methods and treatment, and a bibliography.

Lest there be any tendency on the part of the uninformed to view only the title of this volume and harrumph, "A *state* report—no doubt too provincial to be of general value," let it be pointed out that the variety of minerals produced in California is greater than in any other state and that for a number of these minerals California is an eminent, indeed for some the preeminent, producer among the states (e.g., boron, diatomite, iodine, pumice, quicksilver, sand and gravel, talc, etc.); and it should also be brought out that the coverage, in this volume, even apart from commodities that figure in the state's production, is notably broad and cosmopolitan. For example, though California has never produced nickel, one can find in this volume a well-condensed discussion of the geology of the Sudbury basin in Canada

and an informative treatment of nickel laterization as well. And in the index, under the name of such a far-off country as Burma, are no less than three citations to text discussions. Such broad-gauge treatment is much to be commended. California citizens and California mining interests deserve to have information from far beyond their state borders, for it is highly pertinent in a field with the wide national and international ramifications that characterize the mineral industry today. Coincidentally, this kind of information greatly enhances the all-around usefulness of the volume. In most instances the authors of the various chapters have themselves carried on extensive investigations of the mineral with which they are concerned. The volume is therefore no mere compilation from the literature; along with breadth, it has depth. References show judicious selection, and discussions and citations are for the most part right up to so recent a date as January, 1957. A few "old saws" have survived. One learns that one of "the principal uses" of slate is for school slates. Yet I wonder how many of our readers can remember the last time they saw school slates in use?[1] In view of the wide variety of topics and the considerable number of authors, the editor has succeeded in producing a commendably homogeneous volume. Typographic errors are few and in almost no instances are such as to introduce error or becloud the meaning. A good deal of cross-indexing (from one chapter, to another wherein the commodity concerned is discussed in different aspect) has been introduced and is one of the many helpful features of this new edition. The index itself, despite the criticisms I have made, is exceedingly comprehensive and detailed; and, *greatly* to its credit (this being a subject on which I have strong feelings!), it is all in one piece—one does not need to search in one set of pages for authors, in another for minerals, in a third for localities. Photographs also are included, and are indexed not only by titles, but also by takers. This somewhat novel feature more than compensates for the absence of a "List of Illustrations," such as one traditionally expects to find immediately following the "Table of Contents," in the front of a volume. Full advantage has been taken of the volume's larger format in providing many striking photographs: the diatomite deposits of Lompoc, the Pine Creek tungsten operation of the U. S. Vanadium Corporation, the new open pit of the U. S. Borax and Chemical Corporation—to name but a few of the many that are of interest to the economic geologist. The reference value of the volume could have been improved by specific citations within the text to pertinent photos and diagrams, inasmuch as text in many places is separated from photo by several pages.

Bulletin 176 includes a great deal of technical material, yet this is consistently presented so as to be understandable to the intelligent layman. Thought has also been given to the type of information that will benefit the relatively uninformed, and the would-be prospector and developer. Indeed some passages might well be reproduced on cards and made available for wide distribution. Thus in a discussion of the fact that most minor metals (Ga, Ge, In, Tl, etc.) are recovered from residues, it is brought out that

"although quoted prices of the minor metals range from a few dollars to several hundred dollars a pound, these prices partly reflect the cost of refining, and the producers of the ores commonly receive no payment for the contained minor metals. Many persons who are unaware of this practise and who note that rare metals appear in spectrographic analyses of mineral or rock specimens, are apt to overestimate the value of the material."

[1] Our diving geologists, I understand, are finding slates far superior to ball-point pens for the underwater recording of geological observations; but this new development has as yet had no significant effect on the market.

This volume is a "must" for the reference shelves of good libraries everywhere, and it will likewise be a "must" for students and for professionals in the mineral industries. Where else, within one set of covers, can be readily found such useful and diverse information as, for example, a field test for nickel, the specifications for railroad ballast, a cross-section through a talc mine, a geological map and section of a pegmatite (complete with small gem miner!), a specimen purchase schedule for gold-silver ore, a list of the current uses of germanium, a diagram of the different geologic conditions in which petroleum is trapped in California, the unique procedures for grading and for milling Canadian asbestos, flow sheets for the production of carbon dioxide (whether from natural wells or from alcohol fermentation), an appraisal of the future of cerium, a photograph of off-shore drilling on the Pacific Coast, etc.—and all for the price of only $7.50! The mineral industry owes a hearty vote of appreciation to Olaf P. Jenkins,[2] under whose direction this volume was prepared, to Lauren A. Wright, who must have performed a yeoman task as editor, and to these two men and their twenty-three associates who together provided the authorship for the many illuminating chapters.

IAN CAMPBELL

CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA,
February 14, 1958

Bed Rock Geology of the East Barre Area, Vermont. BY V. RAMA MURTHY. Pp. 121; pls. 33; figs. 9; tbls. 9. Bull. 10, Vermont Geological Survey, Montpelier, 1957.

The East Barre quadrangle is located in the northern portion of Orange County in east central Vermont and lies on the eastern limb of the Green Mountain anticlinorium.

Four lithologic units have been established comprising, from west to east, the Barton River, the Westmore, the Waits River and the Gile Mountain, of which the first two are continuous further north into their type area. Originally they were included in the Waits River formation but the author has shown that due to the excellent mappability of individual units coupled with structural and stratigraphic evidence, they can be separated so that the term "Waits River formation" is now restricted to include only the eastern calcareous unit in the region of Waits River village. The details of these formations are adequately dealt with under the headings: Distribution, Lithology, Thickness, Correlation and Age.

A thorough and careful study of minor structures such as attitude of drag folds and cleavage-bedding relations shows that the area has been subject to two stages of deformation.

In the first stage the rocks were folded into a major syncline with a nearly N-S axis, the trough of which is occupied by the Waits River formation. This indicates that the Waits River formation is the youngest in the Vermont sequence and also that the Westmore formation may be correlated with the Gile Mountain formation. It precludes the hypothesis of a synclinal structure for the Westmore formation which is instead considered to be the western limb of the major syncline, shown up by sinistral drag folds in the argillaceous rocks. On the eastern limb

[2] As this review is being prepared, word comes of the impending retirement of Olaf P. Jenkins, as chief of the State Division of Mines. Impressive as Bulletin 176 may appear as a final contribution under Dr. Jenkins' aegis, a far more impressive measure of his contribution is the index of improvement and progress provided by a comparison of Bulletins 156 and 176.

of the syncline, however, early stage dextral drag folds are scarce, probably due to merging with the second stage deformation.

In the second stage deformation a domal uplift extending from the southern part of the East Barre quadrangle south into the Strafford quadrangle forms the major tectonic element in which the early sinistral folds on the western limb were lifted up and rotated in a counter-clockwise direction with the result that many of them are now recumbent. The early dextral folds in the east limb were affected less, being rotated in a clockwise direction. The main tectonic stress was upwards but with a pronounced northward horizontal component.

Bean's gravity survey of east central Vermont indicating residual negative anomalies associated with domal structures is cited as evidence for granite rising vertically as a plunger. Numerous granite dikes and high-grade metamorphism in the central part of the domal structure render this plausible.

Petrographic studies made on the two major groups of plutons indicate significant mineralogical differences while considerable evidence shows that the Barre granite is magmatic, having been emplaced as a passive intrusion, partly by pushing aside the country rocks and partly by stoping.

Two stages of metamorphism corresponding to the two stages of deformation have been identified, the first, low grade; the second reaching the amphibolite facies. Some contact metamorphism has been noted around the Barre granite and a genetic relationship appears to exist between the metamorphic bodies and the plutons.

ERNEST DECHOW

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February 5, 1958

Prospection Électrique, par Courants Continus. By PIERRE LASFARGUES. Pp. 290; figs. 162. Masson et Cie., Paris, 1957. Price, 3,000 fr.

Equipotential, resistivity, spontaneous polarization, and induced polarization are the subjects of this book. It is written for the geologist and the engineer as an aid in prospecting for minerals, in petroleum investigations, in public works, and in hydrology. The possibilities and the limitations of each method for different kinds of problems are pointed out, as well as variations of each method. The author goes into the theory of each method and particularly develops the interpretation of results. He also describes the potential drop ratio method following the discussion of resistivity. In his discussion of induced polarization, the author states that it is still in a state of preliminary study. However, it has been used in North America for two years. Although some of the methods are used extensively in oil exploration and development, most of the author's illustrations are applied to ore finding and engineering geology. Three pages of references are given, drawn mostly from North America and Europe.

The book is a nice summation of these geophysical methods and is well and clearly illustrated.

The Mineral Wealth of Madhya Pradesh. Vol. 1, No. 1, October, 1957. Pp. 28. Dept. of Geology and Mining, Raipur, India.

This is a new journal and its maiden number. Its purpose is to present information about the mineral resources of this large state in the hope it may stimulate their development. Coal, manganese ore, and cement constitute the largest

mineral industries and these three are briefly described. In addition, iron ore, talc, clays, bauxite, ochres, feldspar, graphite, asbestos, corundum, sillimanite, and diamonds are produced. There is a table of reserves of the different minerals; coal amounts to 5,851 million tons; iron ore, 1,564 million tons; manganese ore 51 million tons and bauxite 12 million tons. There are also sizeable reserves of corundum, sillimanite and ochre. A short paper describes the diamond field of Panna, and this includes the diamond production for the producing countries of the world from 1952 to 1955. A list of the mineral industries of the state and their locations is included.

We extend good wishes to this new journal and hope it serves the purpose for which it was established.

Graphic Methods in Structural Geology. By Wm. L. Donn and J. A. Shimer. Pp. 180; figs. 104. Appleton-Century-Crofts, Inc., New York, 1958. Price, $4.00.

Although this book is intended primarily as an undergraduate text book it can also be used as a reference for graduate students and professional geologists. It presents the common graphic procedures for solving problems in structural geology.

It is divided into 3 parts. Part I is a "Descriptive Study of Bedded Rocks" and deals with horizontal, tilted, folded, and faulted structures, unconformities, and intrusive contacts. Part II takes up "Quantitative Graphic Procedures: Orthographic Projection" such as orthographic projections, structure contours, true and apparent dip, intersecting surfaces, the three point problem, thickness and depth of strata, areal outcrop patterns, lineation and fault problems. Part III, "Stereographic Projections" deals with true and apparent dips from surface and vertical drill-hole data, intersecting surfaces, simple and rotational faults, and problems involving rotation of the sphere of projection about horizontal and inclined axes. An appendix gives the construction of an ellipse, alignment diagrams, and a selected bibliography. The various problems are well illustrated with clearly drawn diagrams and are well chosen. The text is in simple lucid language.

The book should prove to be a good undergraduate text suitable for both explanation and laboratory purposes.

Oil Reservoir Engineering, 2nd Edit. By Sylvain J. Pirson. Pp. 735. McGraw-Hill Book Co., New York, 1958. Price, $14.00.

Two-thirds of this second edition consists of new material that has become available since the 1950 edition. Also this edition contains twice as many illustrations as its predecessor.

The author deals with the fundamental principles of oil recovery from various kinds of reservoir rocks and structures. He emphasizes principles rather than practices. The 14 chapters can be broken down into two sections: one, the steps by which "an evaluation of the original oil in place may be made," and the other "the forecast and control of reservoir performance." The first considers the static reservoir problems, and the second the dynamic problems. The various subjects covered are: reservoir rocks, structures, physical properties, and petrogenesis; electric and radiation logging, and quantitative interpretation of well logs; reservoir-fluid properties and reservoir forces and energies; mechanics of fluid flow in porous media; volumetric evaluation of oil-in-place and empirical reserve estimates; oil production by depletion drive, frontal displacement, water, and segregation drive; and reservoir engineering.

The author gives here his new method of presenting the material balance equa-

tion in finite differences form by which rapid computation of reservoir engineering problems can be made with the use of a slide rule.

This new edition gives very complete information on oil reservoir engineering.

BOOKS RECEIVED

JAMES M. ALLEN AND JOHN W. SALISBURY

The Australian Mineral Industry—Quarterly Review and Quarterly Statistics. Vol. 10, No. 2. Pp. 41; fig. 1; tbls. 19. Price, 3 sh. Bureau of Mineral Resources, Geology and Geophysics, Melbourne, 1957.

Etude Geologique de la Region Matadi Inga—Monolithe. Bull. 7, Fasc. 5. A. BERTOSA and P. THONNART. Pp. 12. Geologic map 1:100,000. Congo Belge, Service Geologique, 1957. *Areal geology, stratigraphy, structure of sedimentary, igneous and metamorphic terrain in the southwest Congo. In French.*

Lead and Zinc in California. J. G. GOODWIN. Pp. 353–758; pl. 1; figs. 8; tbls. 7. Price, $2.00. California Journal of Mines and Geology, Vol. 53, Nos. 3 and 4, San Francisco, 1957. *A complete list of mines by counties preceded by a discussion of the geology, mineralogy, mining, processing, and utilization of lead and zinc in California. Economic mineral (lead-zinc) map of California No. 7, scale 1:1,000,000. Also, complete index to Vol. 53.*

The Geology of the Bui Hydro-Electric Project. L. O. GAY. Pp. 60; pls. 7. Price, 9 sh. Gold Coast Geological Survey Bull 22, Accra, 1956. *Geologic map, scale 1:50,000.*

Topographic Maps of Missouri. T. R. BEVERIDGE, F. C. WHALEY, and L. E. LAMBELET. Pp. 27; figs. 10. Geological Survey and Water Resources Information Circular 15, Rolla, 1957. *Description of uses of topographic maps, map making, and ordering of topographic maps.*

Forty-Fifth Annual Report by the State Inspector of Mines for the Year Ending June 30, 1957. J. A. GARCIA. Pp. 60; pls. 8. Albuquerque, New Mexico, 1957.

Ontario Fuel Board—Third Annual Report. Pp. 151; pls. 4; figs. 5; tbls. 22. Ontario Dept. of Mines, Toronto, 1957. *Report on the natural gas and petroleum industries, exploration and development.*

Historical Statistics of Pennsylvania's Mineral Industries, 1759–1955. JOHN J. SCHANTZ, JR. Pp. 93; graphs 16; tbls. 84. Price, $1.00. The Pennsylvania State University, Bull. of the Mineral Industries Experiment Station, Mineral Conservation Series, Paper I. University Park, Pennsylvania, 1957. *Mineral statistics of historical interest.*

The Mining Laws for Portuguese East Africa (1906–1956). Pp. 111. Serviços de Geologia e Minas, Lourenço Marques, 1957. *Text entirely in English in this version.*

Geology and Mineral Resources of the Gossan Lead District and Adjacent Areas in Virginia. ANNA J. STOSE and G. W. STOSE. Pp. 233; pls. 61; figs. 51. Virginia Division of Mineral Resources, Bull. 72, Charlottesville, 1957. *The Gossan Lead consists of several fissure veins; arranged en echelon, in a mineralized zone extending southwestward for 20 miles across Carroll and Grayson counties. Geologic map, scale 1:62,500.*

Stratigraphy of the Sundance, Nugget and Jelm Formations in the Laramie Basin, Wyoming. GEORGE N. PIPIRINGOS. Pp. 61; pls. 5; figs. 3; tbls. 2. Geo-

logical Survey of Wyoming, Bull. 47, Laramie, 1957. *Restudy of the marine Jurassic formations of the Laramie basin.*

Directory of Geological Material in North America. J. V. HOWELL and A. I. LEVORSEN. Pp. 208. Price, $3.00. The American Geological Institute, Washington, D. C., 1957.

Treatise on Marine Ecology and Paleoecology—Vol. I, Ecology. J. W. HEDGPETH, Editor. Pp. 1,296; pls. 25; figs. 284; tbls. 107. Price, $12.00. The Geological Society of America Memoir 67, Baltimore, Maryland, 1957.

Geophysical Activity 1956. HOMER G. PATRICK. Pp. 18; figs. 10; tbls. 10. Rept. of Standing Committee on Geophysical Activity of the Society of Exploration Geophysicists. *Geophysical activity in the petroleum and mining industry described under: distribution, types of surveys, manpower, money expended.*

Illinois Geological Survey—Urbana, 1957–1958.

Circ. 247. Chitinozoan Faunule of the Devonian Cedar Valley Formation. CHARLES COLLINSON and ALAN J. SCOTT. Pp. 34; pls. 3; figs. 13; tbls. 1. *Description, techniques of collection and preparation of Chitinozoan faunule from single middle Devonian outcrop in northwest Illinois.*

Rept. of Investig. 203. Petrology of the Paleozoic Shales of Illinois. R. E. GRIM, W. F. BRADLEY, and W. A. WHITE. Pp. 33; figs. 6; tbls. 5. *Study of clay mineral content of shales shows illite to be dominant, paolinite variable, and montmorillonite rare in these Paleozoic shales.*

Rept. of Investig. 204. Petrology and Sedimentation of the Pennsylvanian Sediments in Southern Illinois: A Vertical Profile. P. E. POTTER and H. D. GLASS. Pp. 58; pls. 8; figs. 19; tbls. 13. *Petrography, subsurface stratigraphy, sedimentary structures, etc., used to determine provenance and depositional environments of Pennsylvanian sediments in Southern Illinois.*

Rept. of Investig. 205. Pennsylvania Faunas of the Beardstown, Glasford, Havana, and Vermont Quadrangles. HAROLD R. WANLESS. Pp. 59; figs. 2; tbls. 4. *500 species of invertebrate fossils from 49 beds, dominantly marine types, used to infer environmental conditions. Many eustatic sea level changes indicated.*

Indiana Geological Survey—Bloomington, 1957.

Bull. 11. Subsurface Stratigraphy of the Salem Limestone and Associated Formations in Indiana. ARTHUR P. PINSAK. Pp. 61; pls. 5; figs. 8; tbls. 2. Price, $2.00. *The Salem represents three distinct environments; near shore, shelf and basin. Oil production restricted to the shelf facies.*

Field Conference Guidebook 9. Rocks Associated with the Mississippian-Pennsylvanian Unconformity in Southwestern Indiana. Pp. 42; pls. 4; figs. 3. Price, $1.00.

Geological Survey of Japan—Hisamoto-chō, Kawasaki-shi, 1957.

Explanatory Test of the Geological Map of Japan. Moriyoshiyama (Akita-5). ATSUSHI OZAWA and KIYOSHI SUMI. Pp. 47; figs. 8; tbls. 4. Geologic map, 1:50,000. *Areal geology of an area in northeast Japan underlain by Cenozoic lavas and sediments. Gold, copper, sulphur and coal produced. In Japanese; summary in English.*

Rept. 176. Chromite Deposits of Hokkaido. I. Chromite Deposits of the Hidaka-Iburi District. TAKEO BAMBA. Pp. 64; pls. 14; figs. 43; tbls. 2. *Unfaulted deposits occur in vein-like forms in serpentinite. Chromite deposits and country rocks may have consolidated in the same stage, however, as indicated by*

the extension of joint systems developed in the ore bodies, into the surrounding serpentinites.

Bull. 9. Geochemical Survey of Natural Gas in the Vicinity of Shizuoka City. KOJI MOTOJIMA, SHIN'ICHI MAKI, and others. *Studies on the Elastic Wave Velocity in Clastic Rock.* Shozaburo Nagumo. Pp. 72; figs. 52; tbls. 23. *Two papers in Japanese with abstracts in English.*

Bull. 10. *Five papers describing, ground water investigation, an occurrence of lower Triassic limestone, thermal springs, geology of a dam site on the River Sendai. In Japanese with abstracts in English.*

Geological Maps of the Coal Fields of Japan. I. Geological Map and Explanatory Text of the Jōban Coal Field. K. SUGAI, et al. Pp. 154; pls. 6; figs. 58; tbls. 59. *Six geologic maps.*

Distribution of Ground Water in Japan. Geologic map, scale 1:200,000.

Geological Survey of Kansas—Lawrence, 1957.

Bull. 126. Ground-Water Resources of the Ladder Creek Area in Kansas. EDWARD BRADLEY, C. R. JOHNSON, and R. A. KRIEGER. Pp. 191; pls. 11; figs. 21; tbls. 14. *Geology and hydrology of the drainage basin of Ladder Creek in western Kansas. Discussion of irrigation potential and water quality.*

Bull. 127, Pt. 3. The Precambrian Rocks of Kansas. O. C. FARQUHAR. Pp. 119; pls. 10; figs. 4. *Information from subsurface records used to describe type and topography of Precambrian basement rocks. Typical Precambrian metamorphic and intrusive suites present. Description of movement in the basement during at least 4 Paleozoic periods. Excellent map.*

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Economic Geology
Vol. 53, 1958, p. 363

SOCIETY OF ECONOMIC GEOLOGISTS

Meetings

The Annual Meeting of the Society of Economic Geologists will be held in conjunction with the Geological Society of America at St. Louis, Missouri, November 6–8, 1958. Headquarters for the meeting will be the Jefferson Hotel.

Abstracts of papers intended for presentation at the technical sessions must be received by the Secretary of the Society prior to *July 15.* The abstracts should be informative, but they must not exceed the 250 word limit. Authors should submit their abstracts in quadruplicate and should indicate the minimum time needed to present the paper. In the event employer permission to publish is required, the author should certify on the abstract form that the abstract has been cleared for publication.

The Society will also meet and hold technical sessions in conjunction with the American Institute of Mining, Metallurgical, and Petroleum Engineers at San Francisco, February 15–19, 1959. Headquarters will be at the Palace Hotel.

Abstracts of papers to be presented at the technical sessions of the San Francisco meeting must reach the Secretary of the Society on or before *August 15, 1958.* These abstracts should conform with the standards for abstracts set forth above.

Forms on which to submit abstracts can be obtained from H. M. Bannerman, Secretary, Society of Economic Geologists, c/o U. S. Geological Survey, Washington 25, D. C.; or from John H. Melvin, Chairman, SEG Program Committee, 1205 Chartiers Avenue, Pittsburgh 20, Pennsylvania.

Harold M. Bannerman
Secretary
March 24, 1958

Economic Geology
Vol. 53, 1958, pp. 364–365

SCIENTIFIC NOTES AND NEWS

J. B. STONE, general manager of Fresnillo Co., in Mexico has succeeded J. H. ASHLEY who has resigned.

L. A. HAMMONS, formerly with Kiva Explorations, Inc., Austin, Texas, has been named field engineer for Department of Mineral Resources, Phoenix, to cover the northern part of Arizona.

W. F. JAMES was recently named to succeed J. W. STOVEL who has retired from the board of Dome Mines Ltd., Ontario.

HANS A. VOGELSTEIN, president of American Metal Co., was named president of American Metal Climax, Inc., formed recently by the merging of Climax Molybdenum Co. and American Metal Co. A. H. BUNKER, president of Climax, is chairman.

W. D. MCMILLAN, mining engineer and geologist of Denver, Colo., resigned after 17 years with U. S. Bureau of Mines and is now associated with two Denver firms as a consultant.

B. DEWITT MITCHELL, geologist and petroleum production engineer, has been appointed vice president of Yucca Mining & Petroleum Co., Inc., with his office at the company's Albuquerque, N. M., headquarters.

S. P. WIMPFEN has joined Western Machinery Co., San Francisco, as general manager of the planning, research and development department. Formerly he was A.E.C. assistant director of the division of raw materials and manager of the Grand Junction, Colo., office.

E. P. SHEA, head of Butte Mines geological department for the past six years, was recently appointed to the newly created position of chief geologist, Montana Division of Anaconda Co.

W. R. LAHDWEHR retired January 1 as chief geologist and acting manager of Asarco's western mining department. J. F. FROST succeeds him as manager, and W. P. HEWITT, assistant chief geologist, was named senior geologist.

MORLEY ROMANUCK, formerly with Quebec Cartier Mining Co., has joined the W. S. Moore Co., Duluth, Minn.

G. A. BOYD has been transferred from the St. Paul office of Northern Pacific R.R. to a new branch office in Seattle.

ROSWELL W. PROUTY, 67, died January 9 in Pasadena, Calif., after a long illness.

JOSEPH A. BANCROFT, distinguished geologist, whose name has been given to the Copperbelt's youngest producing mine, died on Dec. 11 in Johannesburg at the age of 75.

R. H. KING has been appointed geologist and technical editor of the State Geological Survey of Kansas and associate professor of geology at Kansas University, Lawrence.

J. P. SMITH, previously chief geologist for the U. S. Potash Co., division of U. S. Borax & Chemical Corp., Carlsbad, N. M., is now manager of land and exploration for U. S. Borax & Chemical Corp. in Los Angeles.

A. P. RUOTSALA has joined the geology department of Texas Western College, El Paso, as an assistant professor. Previously he was an instructor in the geology department of Texas Technical College.

H. R. BECKWORTH is serving with the American Exploration & Mining Co., San Francisco, as an engineer in charge of exploration and the Alaskan section.

THE GEOLOGICAL INSTITUTE OF INDIA held its 52nd Annual General Meeting January 19 in the Geology Department, Presidency College, Calcutta. DR. M. CHATTERJEE presided and DR. ATMA RAM, Director, Central Glass and Ceramic Research Institute, was the Guest-in-Chief.

PAUL WEAVER, Professor of Geology, Texas A. and M. College, Houston, received the Sidney Powers Memorial Medal of the A.A.P.G. in recognition of his outstanding contributions to, and achievements in petroleum geology. The presentation was made by ROY R. MORSE. Certificates of Honorary Membership of the A.A.P.G. were presented to CARROLL EDWARD DOBBIN, regional geologist, U.S.G.S., Denver; K. C. HEALD, Fort Worth, Texas; WILLIAM BAYARD HEROY, president, the Geotechnical Corporation, Dallas, Texas; A. I. LEVORSEN, consultant, Tulsa, Oklahoma; RAYMOND C. MOORE, Principal State Geologist, Lawrence, Kansas; and WALLACE E. PRATT, consulting geologist, Carlsbad, New Mexico.

B. D. THOMAS, scientist and research administrator, has been named president of Battelle Memorial Institute to succeed DR. CLYDE WILLIAMS, who retired recently.

H. Z. STUART has been appointed manager of exploration for Phelps Dodge Corp. Formerly he had been resident engineer of mines for Phelps Dodge in New York. This new appointment shifts the corporation headquarters for exploration activities from Douglas, Arizona, to New York.

R. D. FERRON has retired from Kennecott Copper Corp., where he had been in charge of the South American Exploration Department. He has established residence in Los Gatos, Calif., where he is available for consulting work.

C. A. MARK is assistant supervisor, Exploration Division, of the Colombia Iron Mining Co., a subsidiary of U. S. Steel Corp. for exploration in 11 western states. Previously he was geological engineer, Exploration Division, the Colombia-Geneva Steel Division of U. S. Steel Corp.

GLEN A. BOYD has been transferred from St. Paul to the newly opened Seattle office of the Northern Pacific Railway Company's Geology Division.

RAYMOND K. ROBBINS, previously assistant geologist with the Tennessee Coal and Iron Div., U. S. Steel Corp., is now a geologist for the Texas Petroleum Co., Peruvian Div.

D. J. STRAW, who has been on loan for the past two years from Johns-Manville Co. Ltd., Asbestos, Quebec, to Rhodesian Asbestos Ltd., Mashaba, Southern Rhodesia, as chief geologist, has returned to Canada to resume his duties in the Exploration Dept., Canadian Johns-Manville.

E. H. BRINLEY is now employed as resident geologist for the Anaconda Company (Canada) Ltd., at Port Arthur, Ontario, Canada. Formerly he was with Anaconda in Chile, South America.

FRANC R. JOUKIN has been appointed to serve on the Canadian National Advisory Committee on Research in the Geological Sciences.

MURL H. GIDEL, assistant chief geologist for the Anaconda Copper Mining Co. retired in January.

ARTHUR HOREN has been made Director of Raw Materials Division, Universal Atlas Cement Co., New York (U. S. Steel subsidiary). He was formerly with the Raw Materials Division, U. S. Steel Corporation in Pittsburgh.

S. G. LASKY, Staff Assistant for Minerals in the Office of the Secretary of the Interior, was one of the principal speakers at the Institute of World Affairs of the State College of Washington, February 20–22. His subject was "The Realities of Mineral Supply—War and Peace." Other speakers were H. L. KEENLEYSIDE, Director-General of the United Nations Technical Assistance Administration, KINGSLEY DAVIS, United States Representative on the United Nations Population Commission, KARL SAX of the Harvard Arboretum, SAMUEL LIPKOWITZ of the International Bank, and RAYMOND MIKESELL of the University of Oregon.

THE SEVENTH NATIONAL CLAY CONFERENCE will be held on October 20 to 23, 1958, in Washington, D. C., at the U. S. National Museum in the Natural History Building of the Smithsonian Institution and will be open to all who have a common interest in clays and clay technology. It is sponsored by the Clay Minerals Committee of the National Research Council and is under the Chairmanship of Dr. H. F. McMurdie of the National Bureau of Standards. A principal theme for the conference will be "Geology of Clay Deposits." A field excursion is planned for Monday, October 20, to typical clay deposits and soil profiles in northeastern Maryland and northern Delaware. A guided tour to the National Bureau of Standards is being arranged for the afternoon of the 22nd. Complete details of the program will be announced in August.

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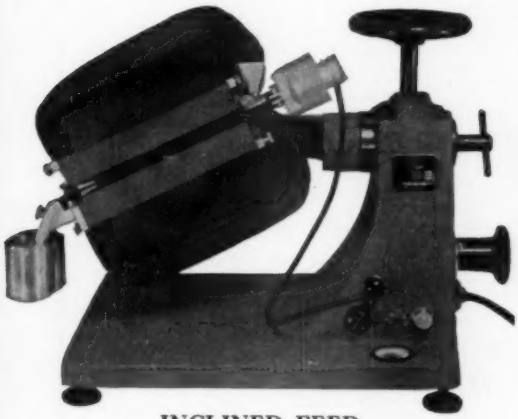

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